Mechanism and Applications of the Photochemistry of Bis(η^5-cyclopentadienyl)titanacyclobutanes

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Do not burn yourselves out. Be as I am-a reluctant enthusiast, a part-time crusader, a half-hearted fanatic. Save the other half of yourselves for pleasure and adventure. It is not enough to fight for the environment: it is important to enjoy it. While you can. While it's still here.

So get out there and hunt and fish and mess around with your friends, ramble out yonder and explore the forests, climb the mountains, bag the peaks, run the rivers, breathe deep of that yet sweet and lucid air, sit quietly for a while and contemplate the precious stillness, that lovely, mysterious and awesome space.

Enjoy yourselves, keep your brain in your head and your head firmly attached to your body, the body active and alive, and I promise you one sweet victory over our enemies, over those deskbound men with their hearts in a safe deposit box and their eyes hypnotized by desk calculators. I promise you this: You will outlive the bastards.

Edward Abbey

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Now that the end is in sight, I would like to thank all those people who have made these last four years not only possible but also rewarding. First I must thank my advisor Bob Grubbs, who gave me freedom when I wanted it and advice when I needed it. It is difficult to imagine working in a better environment. I need to thank my family for support during this little adventure. I want to thank Arvid Lunde for teaching me things that cannot be learned in a lab. I also want to thank the members of the research group past and present who have not only contributed a great deal to my project through advice but who have also made lab an enjoyable place to work. Bill Tumas initiated much of the work detailed in Chapter 1 and Chapter 4. Thanks for not only being a good teacher but also a good friend. I also want to thank the NMR GLA's Doug Meinhart, Eric Ansyln, and Dom McGrath: if it doesn't kill you it, makes you stronger. I must mention those people who proofread this thesis, Gail Ryba, Dom, Eric Ginsburg, Lynda Johnson, LeRoy Whinnery, and Jeff Moore. In terms of research I don't know if I can mention everyone who contributed but I am going to try: Bill Schaefer and Larry Henling for x-ray crystallography, Frank Coms for help with low-temperature ESR experiments, Eric for help with molecular modeling, Tom Dunn for repairing the NMR's and other equipment. Thanks to all the people I went running and cycling with, and the people that I have backpacked with, in particular the Bercaw group, Jim, Leroy, Eric, Tim, and Gail. I also need to thank Frank Cook, whose foresight made my high school and college education financially possible.

Abstract

The photochemically induced reductive elimination of cyclopropanes from bis(η^5-cyclopentadienyl)titanacyclobutanes has been examined. Stereochemical labelling studies indicate that the cyclopropane is initially formed in a 6±1:1, ratio favoring retention of stereochemistry. The starting titanacyclobutane is isomerized during the course of the reaction. The isomerization of the starting material results from metal-carbon bond homolysis to yield a 1,4-biradical, which can either close to give the starting material or generate cyclopropane. The 1,4-biradical can be observed through a cyclopropyl carbinyl rearrangement employing 2-bis(η^5-cyclopentadienyl)titana-5,5-dimethylbicyclo[2.1.0]pentane, to give the titanium alkylidene, 1-bis(η^5-cyclopentadienyl)titana-3,3-dimethyl-1,4-pentadiene, which can be observed directly by NMR at low temperature.

The oxidation of titanacyclobutanes by chemical and electrochemical methods also yields cyclopropanes. Reduction of the metal center does not yield cyclopropanes. Depending on the oxidant, stereochemically labelled titanacyclobutanes yield cyclopropanes that are between 7:1 and 100:1 retention:isomerization. The fragmentation reaction resembles the photochemically induced reductive elimination. Both result from formal oxidation of a metal-carbon bond, which then results in very rapid formation of cyclopropane.

The titanocene generated photochemically reacts with a variety of substrates even at low temperature. Titanocene can be generated in a glass at 77 K. The titanocene can be trapped in noncoordinating solvents in high yield with bulky internal acetylenes to give monoacetylene adducts of

titanocene. Less bulky acetylenes give the titanacyclopentadienes. The titanocene can be trapped with olefins to give less stable adducts, which appear by NMR analysis to be intermediate in structure between a titanacyclopropane and an η^2 olefin adduct of titanocene. Reaction of titanocene with butadiene gives a stable product, which appears to be the s-trans butadiene adduct of titanocene. It does not isomerize on heating. Titanocene reacts with epoxides to give titanocene-μ-oxo polymer and olefin. Stereochemically labelled epoxides and episulfides yield isomerized olefin upon deoxygenation by titanocene. The observations are rationalized as a result of a 1,4-biradical formed by stepwise insertion of titanocene into a carbon-oxygen bond.

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CHAPTER 1

Mechanism of the Photochemically Induced, Reductive Elimination of Cyclopropanes from Bis(η^5-cyclopentadienyl)titanacyclobutanes

Introduction:

This chapter will attempt to detail the photochemistry of bis(η^5-cyclopentadienyl)titanacyclobutanes. In contrast to the well-investigated thermal chemistry[1], the photochemistry has been relatively unexplored. Thermally, bis(η^5-cyclopentadienyl)titanacyclobutanes, also known as titanacyclobutanes, undergo a retro 2+2 cleavage to generate an olefin and a titanocene methylidene. The titanocene methylidene is very reactive and can be trapped in a number of ways. For example, they react via a Lewis acid/Lewis base interaction with phosphines to give a phosphine titanocene methylidene adduct. The titanocene methylidene can undergo 2+2 additions with a variety of substrates. It reacts with olefins to regenerate a titanacyclobutane. It reacts with acetylenes to generate a titanacyclobutene. The titanocene methylidene also reacts with carbonyls in a 2+2 reaction to give a transient α-oxatitanacyclobutane, which then cleaves to yield a methylenated carbonyl and titanocene-μ-oxo. This is a Wittig-like reaction. Perhaps the most important reaction that titanacyclobutanes are known for is ring-opening metathesis polymerization or ROMP. In addition to their thermally induced 2+2 cleavage, titanacycobutanes react directly with a variety of substrates. They react with proton sources to yield alkanes, with bromine to yield the corresponding bromides, and with iodine to yield cyclopropanes, and with acid chlorides to yield titanium enolates. All of these reactions proceed in high yield. Representative examples of the numerous reactions that titanacyclobutanes undergo are shown in Figure 1.

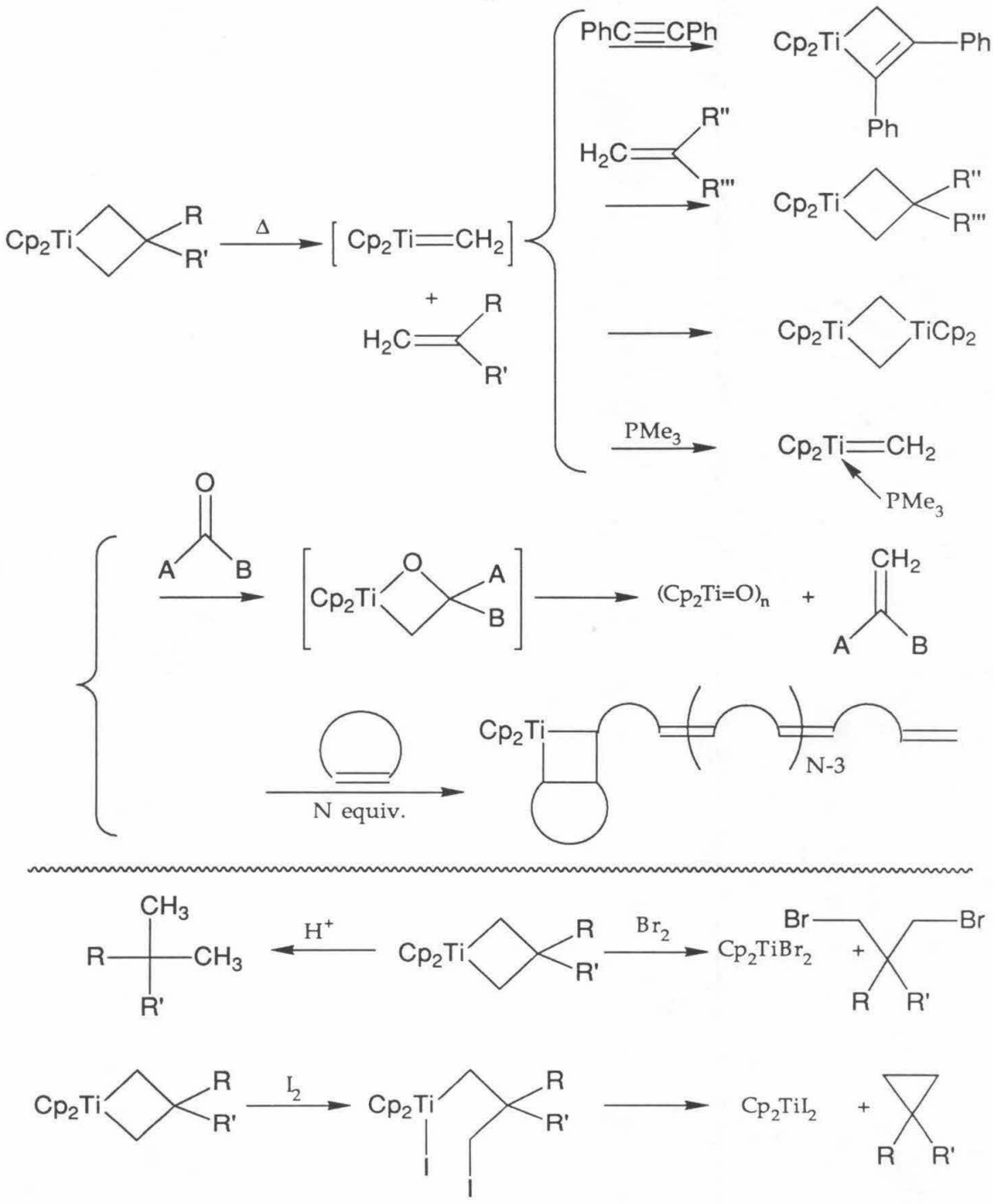


Figure 1. Thermal chemistry of titanacyclobutanes.

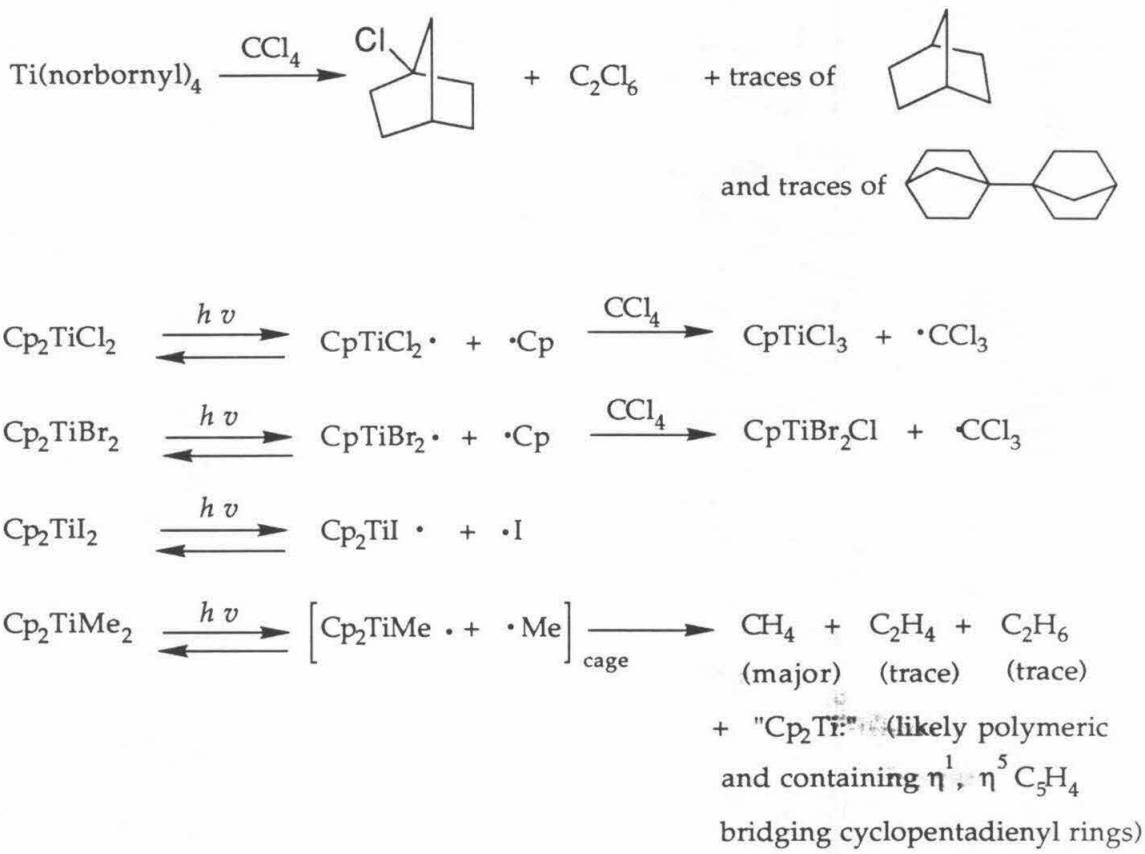
This chapter will examine the photochemistry of bis(η^5-cyclopentadienyl)titanacyclobutanes. The photochemistry of titanacyclobutanes is of interest for many reasons. Photochemistry is often an excellent low-temperature route to extremely reactive intermediates, and it is capable of providing interesting and useful transformations. Additionally, photochemistry often provides clues about the underlying electronic structure of the starting material. While organometallic photochemistry is not as well investigated as organic photochemistry, it is a clearly expanding area, and there are increasing numbers of examples of each of these various reactivities.

Historically, there have been few investigations of metallacycle photochemistry. However, the investigations that have been undertaken have hinted at interesting and potentially useful chemistry. A series of platinacyclobutanes has been investigated by Puddephatt and coworkers.[2] Depending on the solvent, the primary organic products were cyclopropane and propene. In low dielectric solvents the initial photoreaction was determined to be β-elimination followed by reductive elimination to propene. In dimethylsulfoxide, cyclopropane yield increased when the photolysis was performed in the presence of a trans-labilizing ligand. The reaction mechanism presumably involved photoinduced heterolytic disassociation of a halide, followed by coordination of the trans-labilizing ligand which then facilitated the reductive elimination.

The photochemistry of a number of tungstacyclobutanes was investigated by Green and coworkers.[3] The organic products of the reactions were very complicated. They included propenes, cyclopropanes and ethylene, as well as traces of other products. The organometallic products were not determined, and primary photoprocesses were not

separated from secondary photochemistry and thermal chemistry. Nonetheless, the organic products hint at exciting chemistry. The ethylene produced suggests that cyclobutane undergoes a retro 2+2 cleavage to give a tungsten methylidene. The propenes in the product mixture indicate that photochemical β-elimination, followed by thermal reductive elimination is likely to have occurred. The cyclopropanes could be formed by reductive elimination. Reductive elimination implies that tungstocene was likely an intermediate. These results are in contrast to the chemistry of dimethyl tungstocene, which upon photolysis yielded products indicative of loss of methyl radicals.[4] Photochemical routes to tungstocene would allow the chemistry of this reactive material to be examined at low temperature. Photochemical 2+2 reactions could provide routes to new olefin metathesis catalysts that could be controlled photochemically.

While there have been no studies of early metal metallacyclobutane photochemistry besides Green and coworkers', the photochemistry of the related early metal alkyls has been extensively explored. The results are quite controversial, but a general consensus is slowly being reached. A review of the photochemistry of titanium alkyls is presented in Figure 2. Photolysis of tetraneopentyltitanium and tetranorbornyltitanium is best characterized by metal carbon homolysis in a solvent cage.[5] However, photolysis of tetraneopentyltitanium and tetranorbornyltitanium yielded traces of coupling products 2,2,5,5-tetramethylhexane and binorbornyl, respectively, in addition to the expected neohexane and norbornane. This observation cannot be accounted for by a simple solvent cage model.



The hydrogen incorporated into the methane comes predominately from the Cp rings of Cp_2TiMe_2

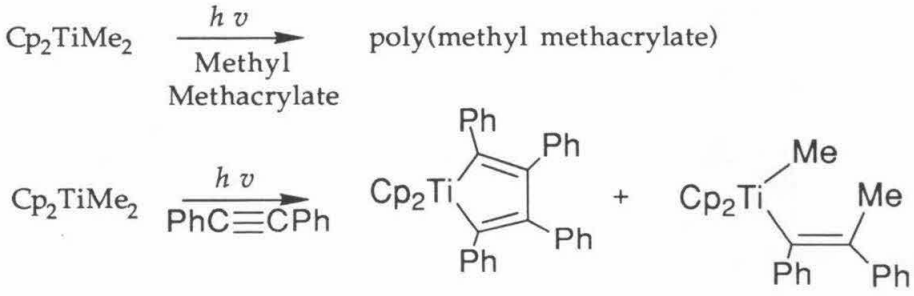


Figure 2. Review of acyclic early metal alkyl photochemistry.

Replacement of two of the alkyl ligands of the tetraalkyltitanium species with two cyclopentadienyl ligands complicates the photochemistry further since there are now two different types of ligands on the titanium metal center. Despite this added complication, it is illustrative to review the photochemistry of the bis(cyclopentadienyl)titanium, compounds since they are more closely related to the bis(cyclopentadienyl)titanacyclobutanes. While it is expected that the photochemistry of titanacyclobutanes will be significantly different from that of the dialkyls, the titanocene dialkyl photochemistry provides a basis to understand the photochemistry of the analogous cyclic material.

Photolysis of dimethyltitanocene in aliphatic solvents yields methane and traces (<1%) of ethane and ethylene. The organometallic product reacts as one would expect titanocene to, but is likely oligomeric with bridging η^1, η^5–cyclopentadienyl ligands. Labelling studies indicate that the hydrogen incorporated into the methane comes predominantly from the cyclopentadienyl ring. This result was also observed in toluene, suggesting that methyl radicals are not formed, since they would be expected to abstract hydrogen atoms from the solvent to form benzyl radicals.[6] However, photolysis of dimethyltitanocene in the presence of the radical traps 5,5-dimethyl-1-pyrroline-N-oxide and nitrosodurene provided ESR signals indicative of methyl radicals.[7] Additional evidence for extremely short-lived methyl radicals was gained by the observation of CIDNP signals when bis(methylcyclopentadienyl)dimethyltitanocene was irradiated in the presence of traces of oxygen.[8] Work by Van Leeuwen and coworkers indicated that the geminate radical pair was extremely short-lived, on the order of diffusion control. This observation of an extremely short-lived radical pair reconciles the earlier results, which seemed to indicate that

methyl radicals were not formed. A summation of the photochemistry is shown in Figure 2.

Photolysis of diphenyltitanocene in perdeuterobenzene gives an equal yield of d_0-biphenyl and d_5-biphenyl. This indicates that both phenyl metal bond homolysis and reductive elimination are occurring simultaneously.[9] Erker has demonstrated that biphenyl is the only product observed from the photolysis of diphenylzirconocene. Diphenylzirconocene is isoelectronic with diphenyltitanocene. This result suggests that for diphenylzirconocene the reductive elimination is concerted. Diphenylzirconocene is often used as a photochemical source of zirconocene.

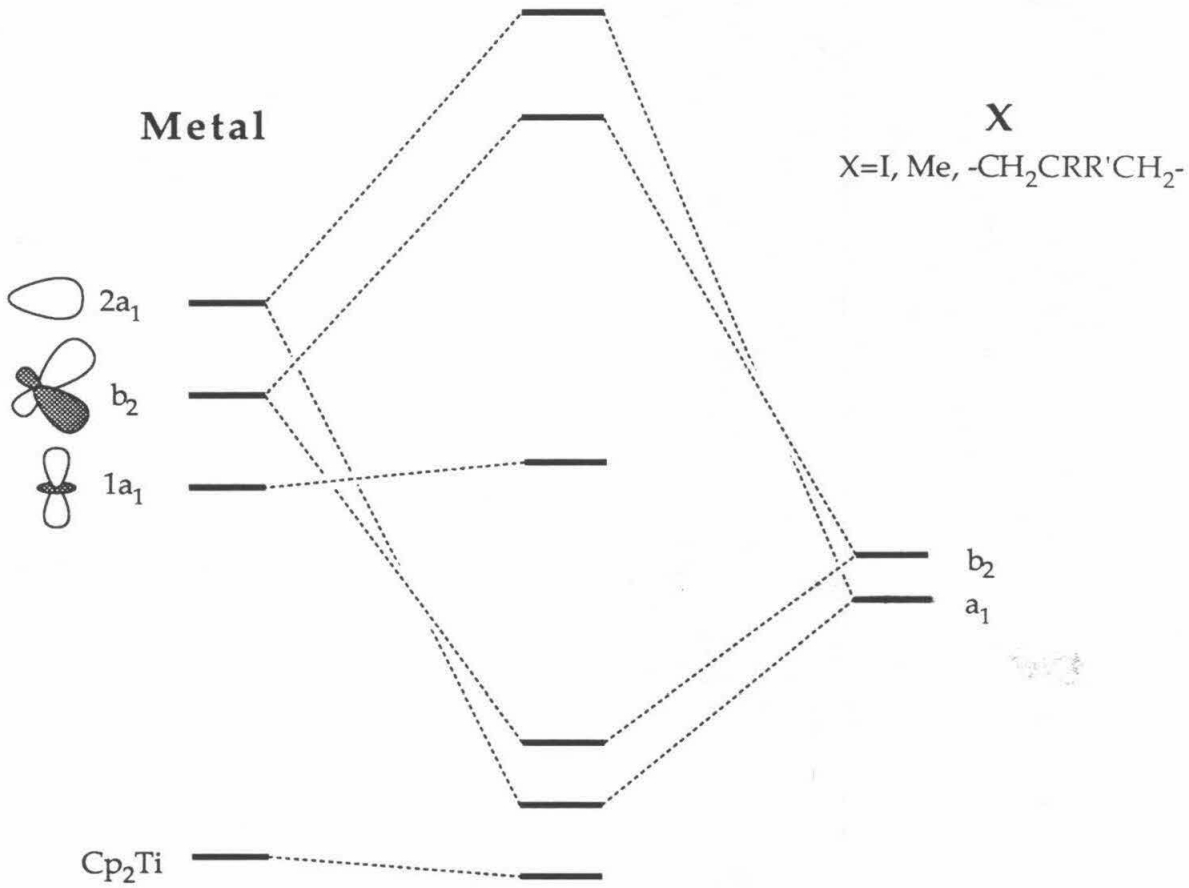


Figure 3. Simplified molecular orbital diagram of $Cp_2Ti(X)_2$.

In order to understand the photochemistry of the titanocene dialkyls and dihalides, one must understand the electronic structure of $Cp_2Ti(X)_2$. The electronic spectrum of a series of titanocene derivatives has been assigned.[10] The assignment is based on both calculation and experimentation. The HOMO for $Cp_2Ti(X)_2$ when X is equal to halide was calculated to be predominantly cyclopentadienyl and titanium in character. The LUMO was calculated to be primarily an empty d orbital on titanium.

Significantly, the cyclopentadienyl-metal orbitals and halide-metal orbitals become closer in energy as X changes from fluoride to methyl. The energy differences decrease in the following order: F > Cl > Br > I > methyl. It was suggested that these orbitals may even exchange places; this exchange would change the HOMO from the Cp-metal orbital to the halide-metal orbital.[11] Experimental evidence supports this exchange. Photolysis of Cp_2TiF_2 and Cp_2TiCl_2 results in loss of a cyclopentadienyl ring, probably initially as cyclopentadienyl radical.[12] Photolysis would excite a ligand to metal charge transfer (a ligand to metal charge transfer was calculated to be the lowest energy transition), which would weaken the metal-Cp bond. The LUMO is predominantly nonbonding. Changing X from fluoride, chloride or bromide to iodide or methyl results in a transposition of the orbitals, and now the HOMO is metal-X in character and the photolysis causes metal-X bond homolysis. This orbital picture, while admittedly simple, helps explain some basic observations of the photochemistry. These simplified molecular orbital diagrams are shown in Figure 3 and Figure 4.

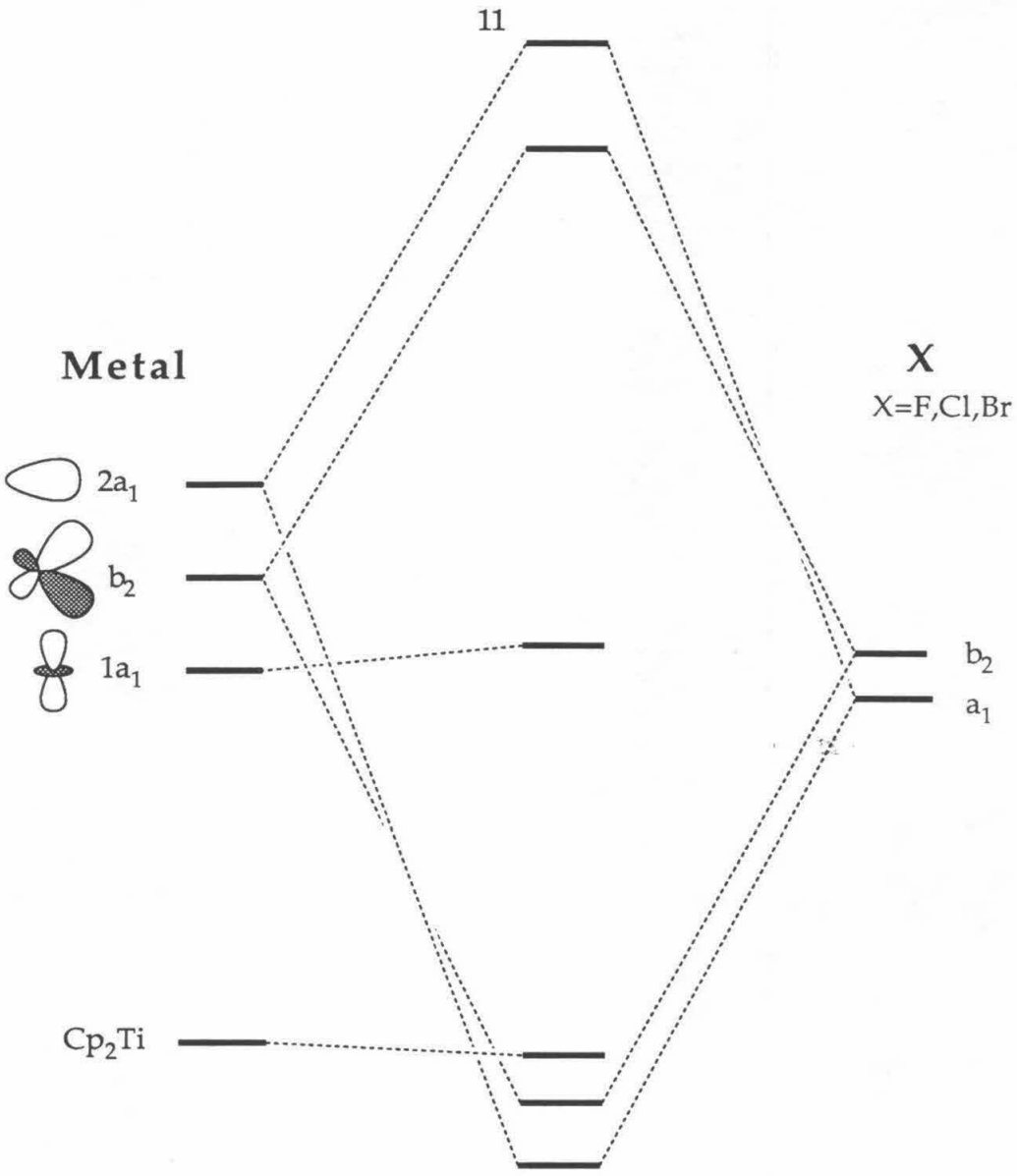


Figure 4. Simplified molecular orbital diagram for Cp_2TiX_2.

An investigation of the photochemistry of the bis(η^5-cyclopentadienyl)titanacyclobutanes was undertaken to define more fully their electronic structures. This knowledge would then prove useful for understanding current and developing new, olefin metathesis catalysts.

Besides gaining a greater fundamental understanding of early metal metallocene photochemistry, there are numerous other reasons to examine the photochemistry of bis(η^5-cyclopentadienyl)titanacycles. First, the bis(η^5-cyclopentadienyl)titanacycles encompass a diverse range of compounds, many of which are important synthetic and catalytic materials. Second, the thermal chemistry of titanacyclobutanes is very well understood, the chances of separating thermal chemistry from primary photochemistry will be greater. Third, an increased understanding of the intrinsic nature of titanacyclobutanes may provide opportunities to better exploit their chemistry. Perhaps new compounds and new transformations will be discovered through an exploration of the photochemistry. Fourth, since bis(η^5-cyclopentadienyl)titanacyclobutanes are tetravalent, they are formally d^0. This simple electronic structure means that unlike the late metal systems, only simple excited states are present. For example, in the absence of a large spin-orbit coupling, one may expect to observe only singlet and triplet excited states. Fifth, dialkyl titanocene photochemistry has been fairly well investigated. Therefore, the effect of the cyclic nature of the starting metallacycle on the photochemistry can be directly addressed. As in organic photochemistry, there are dramatic differences between cyclic and acyclic materials. Lastly, the synthesis of titanacyclobutanes readily allows one to introduce deuterium labels. This means that mechanistic investigations are fairly straightforward. While not all of the above scenarios were realized, many interesting observations were made during the course of examining the photochemistry of the titanacyclobutanes, and these observations will be detailed in the subsequent section.

Results and Discussion:

Early examination of the chemistry of titanacyclobutanes by Kevin Ott of our research group revealed that photolysis of bis(η^5-cyclopentadienyl)titanacyclobutanes generates cyclopropanes.[13] After this initial observation, a more thorough investigation was undertaken. In order to determine the reaction mechanism a series of photochemical experiments were undertaken. These experiments included labelling studies, an examination of the secondary deuterium isotope effects, an extended study of solvent effects on the photochemical products and stereochemical product distribution, low-temperature matrix photolysis, low conversion experiments, qualitative quantum yields, examination of additional titanacycles, and trapping studies.

After initial observation that titanacylobutanes cleanly and in high yield reductively eliminated cyclopropanes upon photolysis, studies were initiated to determine the mechanism of the reductive elimination. Deuterium labelling studies provided an elegant means of doing this. Incorporation of stereospecifically deuterated olefins into the titanacycles is a relatively straightforward task. Photolysis of these labelled metallacycles generated cyclopropanes with partial retention of the initial stereochemistry. A concerted mechanism would be expected to generate a cyclopropane that would mirror the stereochemistry of the starting metallacycle. A stepwise mechanism would be expected to generate cyclopropanes with a scrambled stereolabel. Both of these mechanisms are shown in Figure 5.

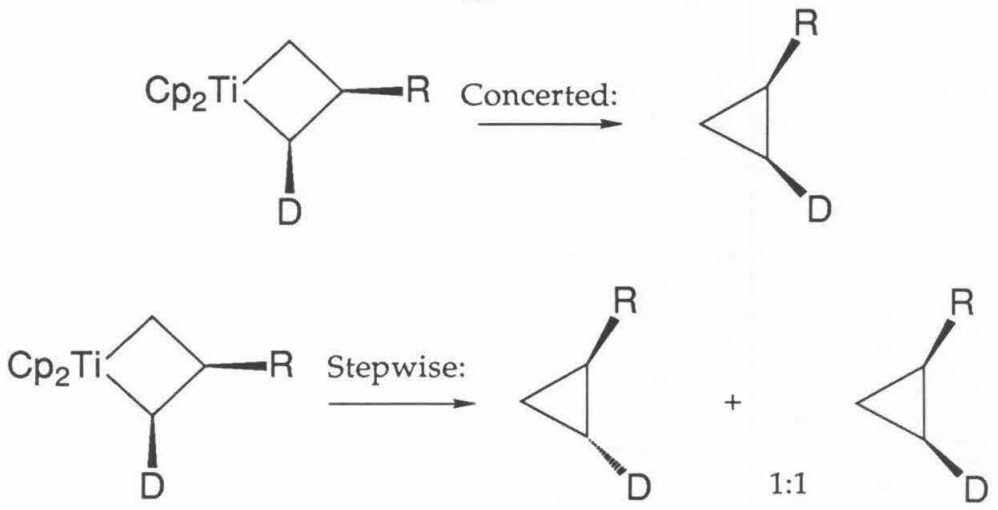


Figure 5. Stereochemical effects of concerted and stepwise reductive elimination.

The initial product upon photolysis of a stereolabelled titanacyclobutane is cyclopropane with a stereochemical ratio of 5.5±1.0:1 retention of stereochemistry:isomerized stereochemistry. Significantly, the stereochemistry of the starting metallacycle was slowly lost during the course of the photolysis. The final stereolabel distribution in the cyclopropanes was 3:1. Since neither total retention nor total scrambling of the stereolabels was observed, the mechanism of the reductive elimination could not be just stepwise or concerted.

Had photolysis generated any titanocene methylidene, it would have been intercepted by diphenylacetylene (one of the many traps used). The would-be product, bis(η^5-cyclopentadienyl)titanacyclobutene has been investigated independently and has been shown to be photochemically inert under the reaction conditions. Additional control experiments demonstrated that the stereochemical results were not a function of starting material. A range of differently substituted and differently labelled titanacycles were synthesized and found to behave in an identical fashion. Titanacycles with β-*tert*-butyl and β-isopropyl substituents were synthesized

with stereolabels.[14] Compounds with deuterium both cis and trans to the β substituent were synthesized for both of the different β substituents. Additionally, a series of compounds with the remaining β position deuterated was also synthesized. The stereochemistry was also unaffected by starting material concentration or trap concentration or the nature of the trap.[15] Traps that were investigated for their effect in stereochemical experiments included trimethyl phosphine, diphenylacetylene, and dimethylacetylene. Concentration effects were found to be nonexistent. The reaction was performed with a range of 1 to 10 equivalents of trap without affecting the stereochemical outcome. Additionally, Lewis acid catalyzed isomerizations (titanocene is Lewis acidic) were not involved. A labelled metallacycle in the absence of a trap was photolyzed to 50% conversion. After 24 hours at -20 °C in the dark, no changes in the stereochemistry of the metallacycle or the cyclopropane were observed. This observation implies that the reaction conditions cannot be responsible for any isomerization of the metallacycle or cyclopropane.

The isomerization of the starting metallacycle was explained by reversible metal-carbon bond homolysis. The absence of solvent effects (toluene, tetrahydrofuran, acetonitrile, and carbon disulfide) on the stereochemistry of the product or the rate of isomerization of the starting material suggests that charge-separated species are not involved. Additionally, it is known that photolysis of early metal alkyls produces radicals. Reversible metal-carbon bond homolysis implies the existence of a metal-centered 1,4-biradical intermediate.[16] However, this titanium-centered 1,4-biradical does not necessarily lie on the pathway to the cyclopropane. While it was relatively straightforward to explain the isomerization of the starting metallacycle, explanation of the

stereochemistry of the cyclopropane produced was more difficult. Additional photochemical experiments were undertaken to probe this question.

In a typical experiment, at 10% conversion of the starting material to cyclopropane, the cyclopropane stereochemistry was 5.5±1:1 retention to isomerization. At 10% conversion the stereochemistry of the starting metallacycle was 30:1 retention of initial stereochemistry to isomerized stereochemistry, down from >50:1 prior to photolysis. In order to explain the stereochemistry of the cyclopropane, the mechanism in Figure 6 was proposed and examined. In this mechanism a differentiation of metal carbon bonds is realized through a secondary kinetic isotope effect. The isotope effect favors cleavage of titanium-CH_2 bond over the titanium CHD bond. The methods of introducing stereochemical labels into titanacyclobutanes provide only unsymmetrically labelled starting materials. The secondary isotope effect was used to explain the abnormally large amount of retention observed. Figure 6 also shows how an isotope effect would change the 3:1 branching ratio to the 5.5:1 observed ratio. One pathway leads to all retention, the other to a 1:1 ratio of retention to isomerization. The isomerization pathway requires that bond rotation of the bond bearing the stereolabel be fast relative to closure of the biradical. Although most S_H2 reactions proceed with inversion, backside attack to give inversion is not observed here.[17] If this mode of attack were taking place, it would require numerous carbon-carbon bond rotations to achieve a position where the carbon-centered radical could backside attack the α-carbon. The time required for so many carbon-carbon bond rotations would result in total scrambling of the stereochemistry. This backside mode of attack is not compatible with the branching mechanism shown in Figure 6.

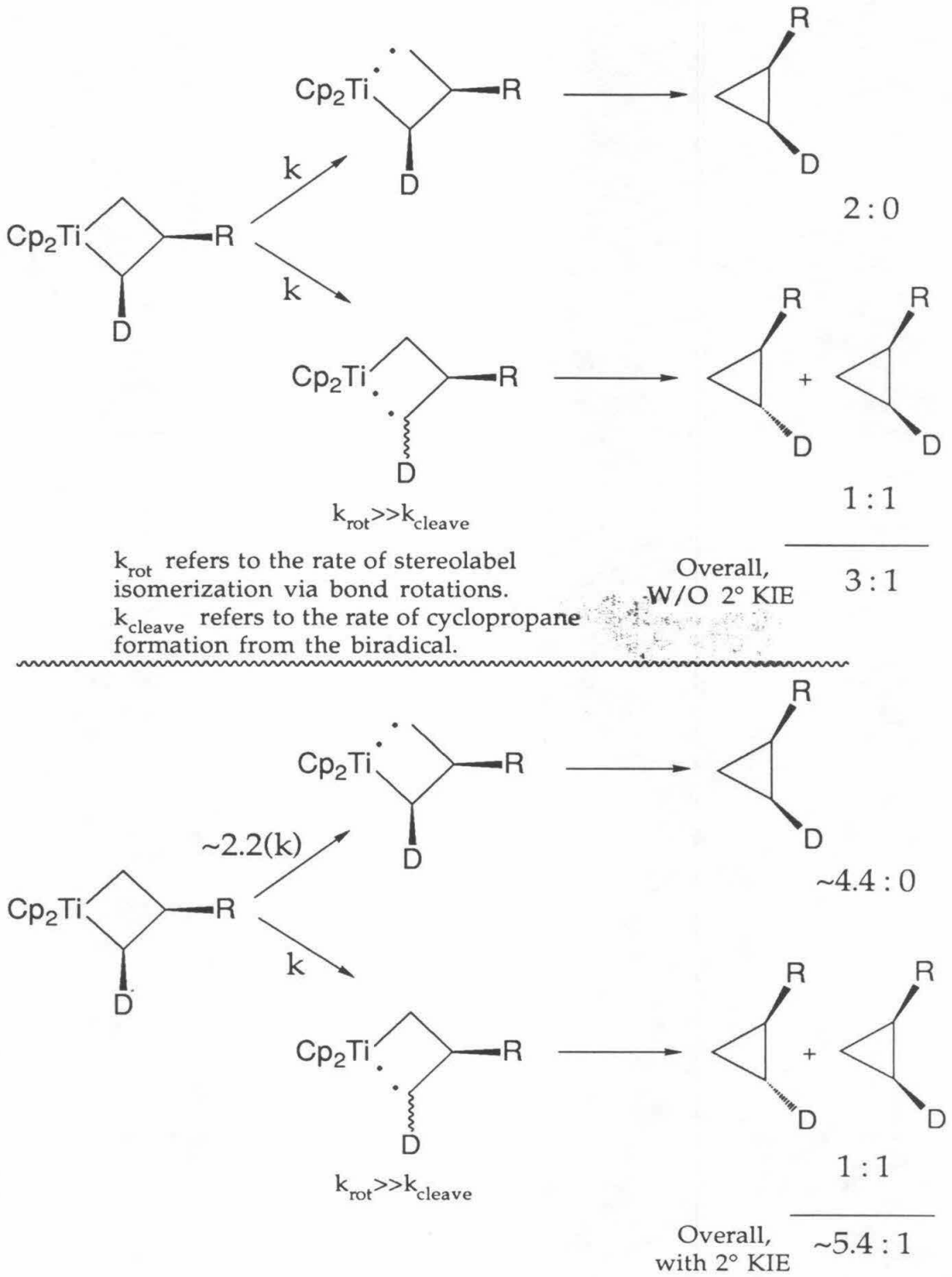


Figure 6. Branching mechanism with and without a secondary kinetic isotope effect.

The nature of the secondary isotope[18] effect shown in Figure 6 stems from the fact that the α carbons bonded to the deuterium prefer to remain sp^3 hybridized, not sp^2 hybridized as they would be in the postulated 1,4-biradical. This means that the metal-carbon bond without the stereolabel is the one most likely to be broken. This translates into an increase in retention in the isomer ratio of the cyclopropanes. Typical values for secondary isotope effects for reactions in which deuterated carbon atoms undergo hybridization changes can be as large as ~1.4. The large isotope effect invoked in the mechanism in Figure 6 could result from the low temperature at which the reaction is performed and/or from a transition state that is very late on the reaction pathway.

Measurement of the secondary isotope effect was critical to the validation of the postulated mechanism. In order to measure the secondary isotope effect, it was decided to synthesize a titanacyclobutane in which a proton carried the stereochemical label, that is to say, a titanacyclobutane that was dideuterated on the alpha carbon without the stereochemical label. The target titanacyclobutane is shown in Figure 7. It should be noted that the β position of the titanacyclobutane was also deuterated. This additional label ensures no interference between the NMR resonance of the starting titanacyclobutane and the cyclopropanes formed.[19] This material would provide a very sensitive probe of the secondary isotope effect, since the isotope effect would be expected to yield more isomerized material than the 3:1 ratio that Figure 6 depicts. An isotope effect of 2.2 as postulated in Figure 6 would result in an initial ratio of cyclopropane stereochemistry retention:isomerization to be ~1.9:1.0, a large change from 5.5 to 1. The mechanism of this isomerization from an initial 5.5:1 to ~1.9:1.0 is shown in Figure 7.

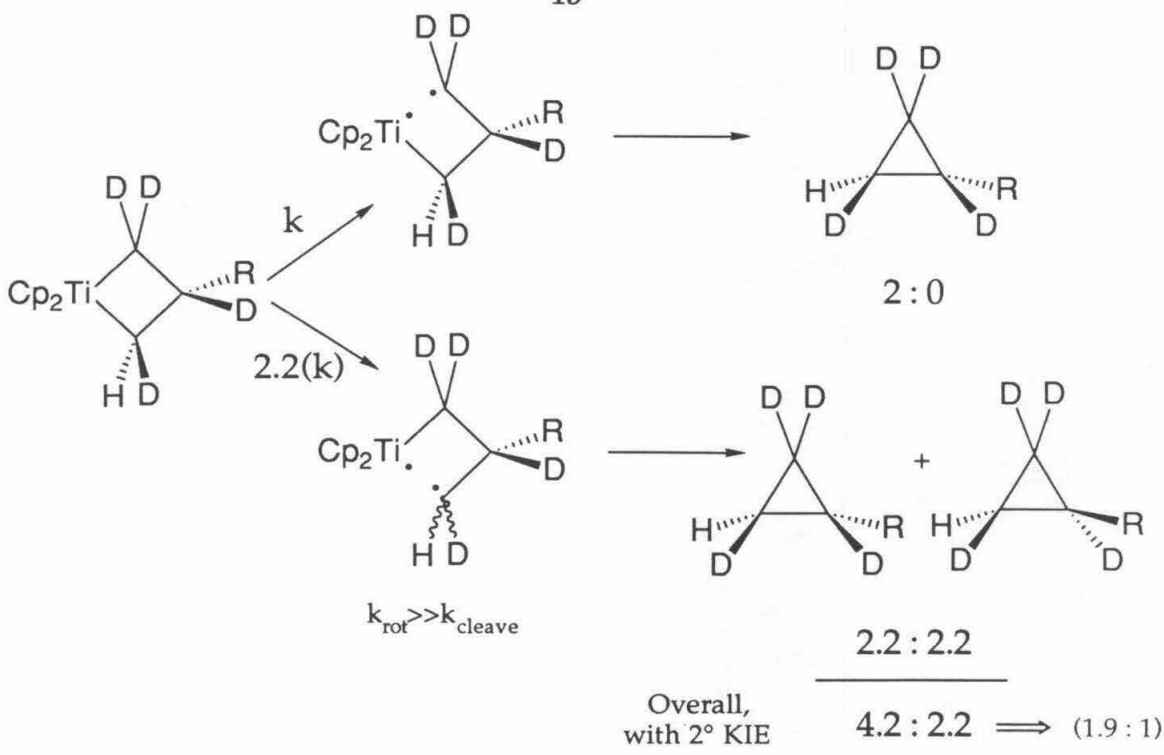


Figure 7. Method to measure secondary kinetic isotope effect. Since the stereolabel is now on the less deuterated α carbon, it should cleave preferentially due to the secondary kinetic isotope effect. More isomerization should be observed from cleavage of this carbon.

Two different synthetic routes were pursued to obtain the desired tetradeuterotitanacyclobutane. The first and the simplest synthesis was to wash deuterium into the alpha positions of a metallacycle via exhaustive olefin metathesis as shown in Figure 8. This method was partially successful since it did provide a small amount of the perdeuterated ß,ß-dimethyltitanacyclobutane. This compound was successfully converted to the final target molecule shown in Figure 7. This exhaustive metathesis route resulted in low yield because of side reactions such as the irreversible dimerization of the titanocene methylidene to 1,3-dititanacyclobutane. Additionally, the large isotope effect, which favors protons on the titanium methylidene, required large amounts of deuterated olefin.

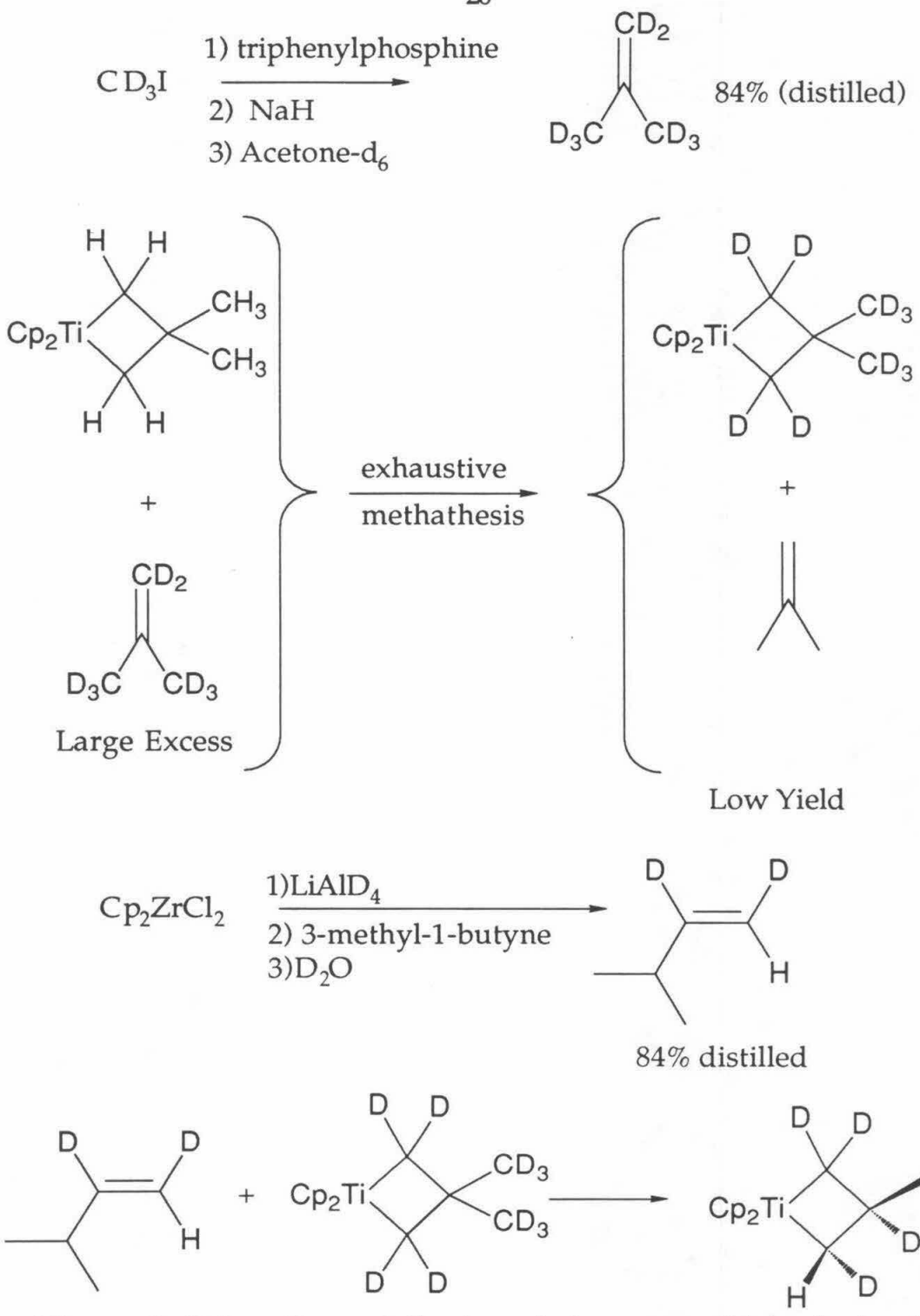


Figure 8. Exhaustive metathesis route to an α,α,α,β-tetradeuterated titanacyclobutane.

In order to overcome these problems as well as others, a more direct synthesis was undertaken. The reactions employed are shown in Figure 9. The step in which the stereospecifically labelled olefin is introduced into the perdeutero-metallacycle is particularly difficult, since dimethyl aluminum chloride catalytically scrambles the stereolabels. This meant that extremely careful recrystallization of the thermally sensitive decadeutero ß,ß-dimethyltitanacyclobutane was required. In the final product the isotope enrichment was 25:1. While this is somewhat low as compared with the other stereolabelled metallacycles, it reflects the large isotope effect disfavoring deutero methylidenes that one encounters throughout the synthesis. Nonetheless, the level of enrichment was more than adequate to address numerous questions associated with this material.

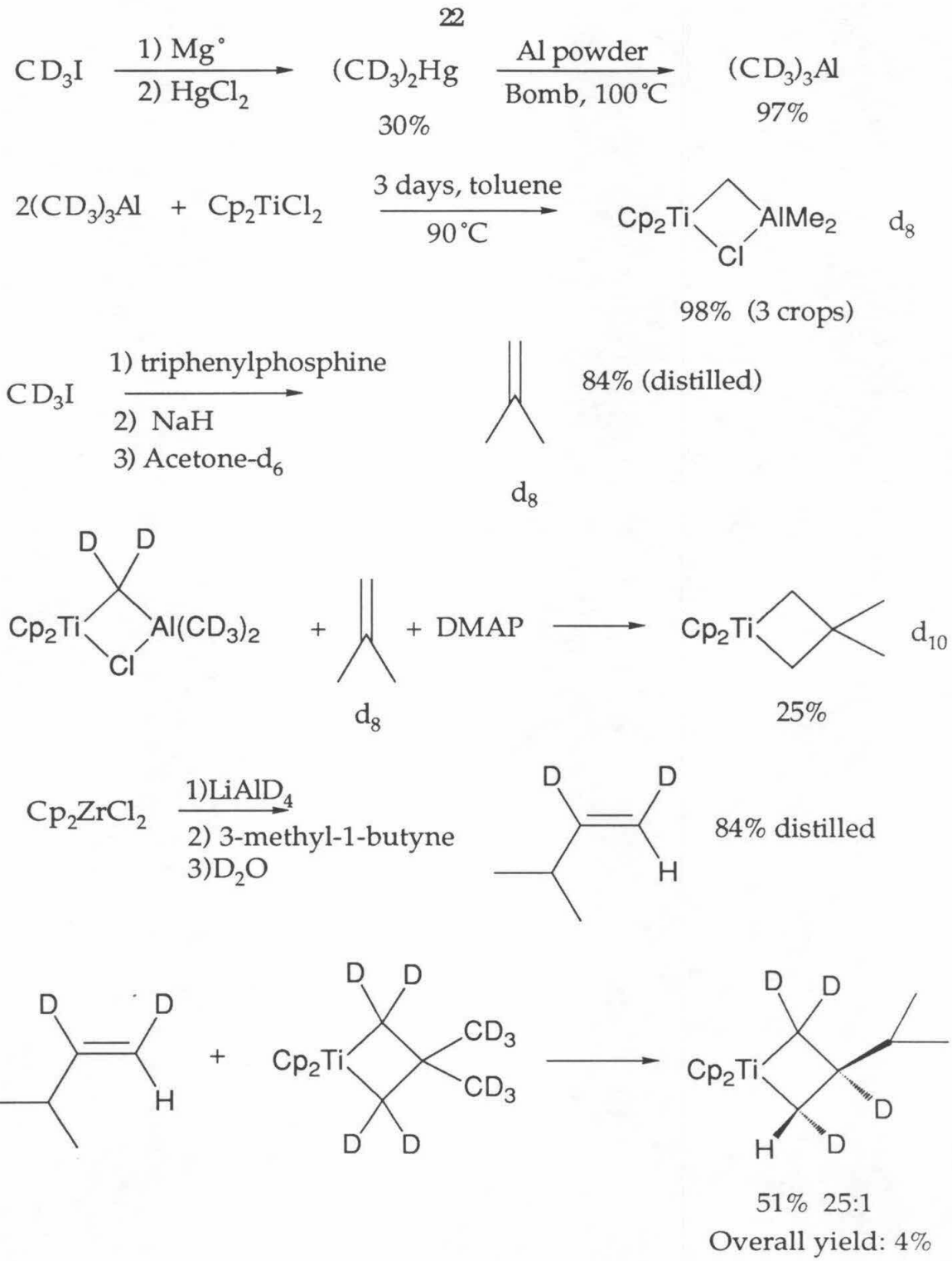
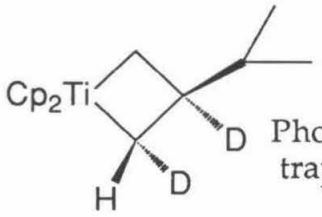
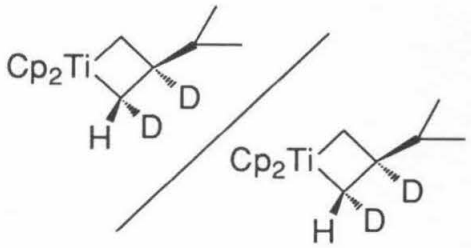


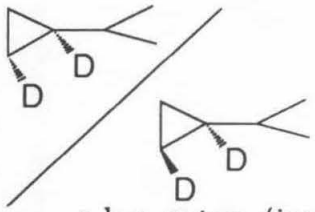
Figure 9. Efficient synthesis of the α,α,α,β tetradeuterated titanacyclobutane.

The first series of experiments with this compound was aimed at measuring the secondary kinetic isotope effect. Surprisingly, photolysis of the tetradeuterotitanacyclobutane in both THF and toluene with a variety of different traps, (2-butyne, diphenylacetylene, and trimethylphosphine, and without traps) yielded the exact same stereochemical results as were obtained with the monodeuterated titanacyclobutanes within the error bars associated with the integration of NMR signals. This result invalidated the mechanism shown in Figures 5, 6, and 7. There was clearly no large change in the stereochemical ratio of the cyclopropanes upon changing from the α-deutero to the α,α,α-trideutero titanacyclobutanes. There may actually be a small amount of extra retention in the cyclopropanes formed from the α,α,α,β-tetradeutero-β-isopropyltitanacyclobutane. This would be indicative of an inverse secondary kinetic isotope effect. The data from a series of stereochemical experiments are shown in Figure 10.



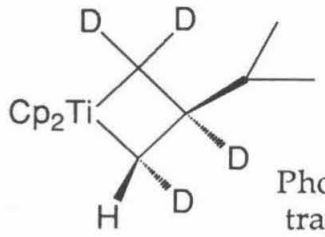
Photolysis in THF or Toluene
trapped with diphenylacetylene.



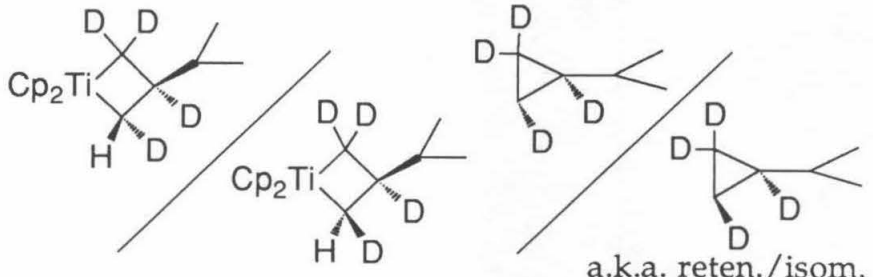


Exent of Reaction (%)		a.k.a. reten./isom.
0	>50/1	–
10	30/1	5.5/1
26	8/1	4.6/1
58	3/1	4.0/1
76	1.7/1	3/1
88	1.3/1	3/1

Figure 10a. Data from typical stereochemical experiments.



Photolysis in toluene
trapped with diphenylacetylene.



Exent of Reaction (%)		a.k.a. reten./isom.
00.0	36.5	-
14.2	12.5	7.8
27.0	8.1	5.9
35.6	6.8	5.8
43.9	4.9	5.4
51.9	3.6	4.5
61.0	3.1	4.4
77.1	2.8	3.3
87.1	1.2	3.1
93.7	0.9	3.0

Figure 10b. Data from typical stereochemical experiments.

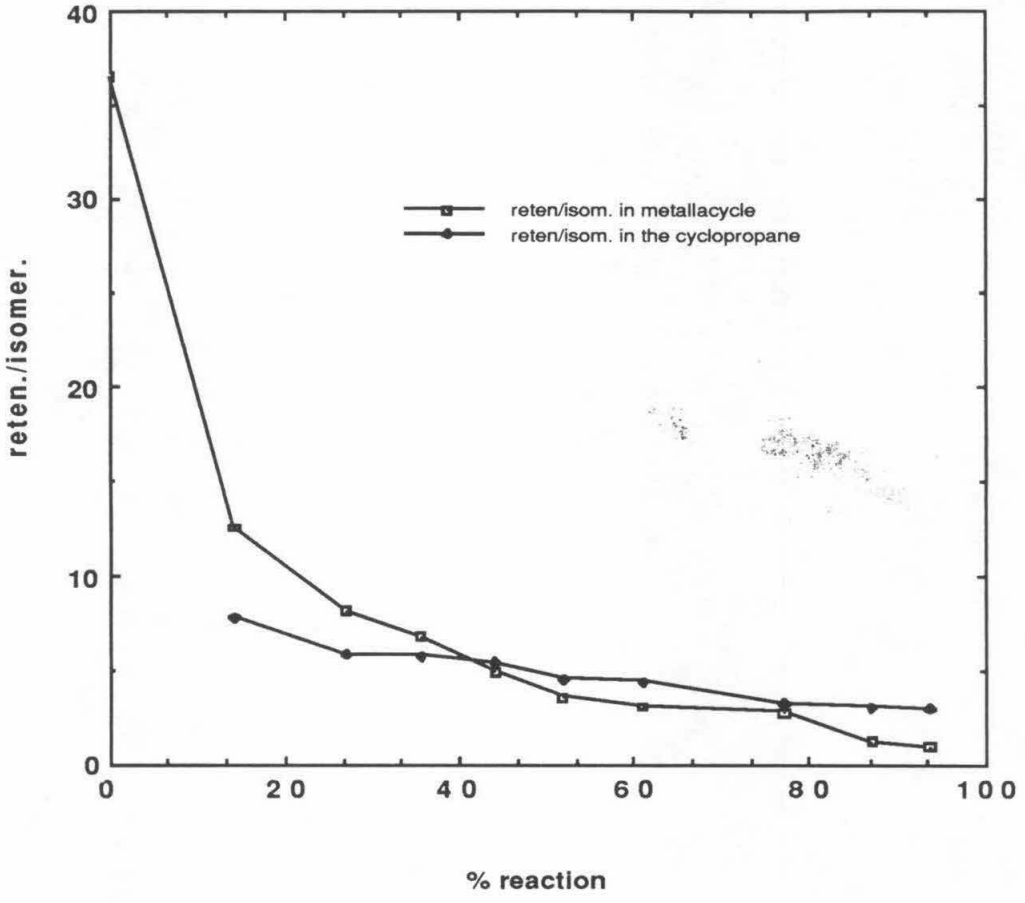


Figure 10c. Graphic representation of data from Figure 10b.

The error in the integrations are fairly large despite the standard precaution of using small tip angles, long acquisition times, and long pulse delays. The errors are especially great early and late in the reaction when large signals are compared to small signals in order to determine the extent of reaction. The extent of reaction was calculated from the ratio of the isopropyl signals for the starting titanacycle against the signals for the isopropyl group of the cyclopropane. Additionally, it was calculated from the ratio of cyclopropane resonances and metallacycle alpha proton resonances against an internal standard. Loss of mass during the course of the experiment was not observed. Additional problems associated with the integration arise from the monodeuterated titanacyclobutanes. To examine this material by proton NMR requires one to measure stereochemical ratios in the following manner. A 2:1 ratio of cis α protons to trans α protons indicates 100% pure stereoisomer. A 1:1 ratio of cis α protons to trans α protons indicates a 50/50 mixture of stereoisomers. Therefore, an integration change of only 33% spans the entire range of stereoisomer ratios that are encountered. The same is true of the integration of the cyclopropane resonances. Deuterium NMR avoids this problem, but it suffers from low sensitivity and broad lines (especially difficult in this situation, since the chemical shift differences are so small between the different stereoisomers of both the starting materials and the product, cyclopropanes) and suffers from the inability to shim or lock the sample. The inability to shim causes broad lines, while the inability to lock the sample means that the length of time that one can acquire the spectrum is limited to the quotient of the natural line width of the signal and the rate of frequency drift of the magnet (typically, 1 Hz/(1 Hz/hr)=1 hr maximum

accumulation time). Despite these problems, the combination of deuterium and proton NMR sets error limits on what the actual values were.

The absence of the secondary kinetic isotope effect meant that the branching mechanism in Figure 6 could not be solely responsible for the product distribution observed. It must be emphasized that the absence of a secondary kinetic isotope effect does not rule out this branching mechanism, it merely indicates that something else must also be taking place to generate as much retention as is observed. The most plausible and simplest way to rationalize the additional retention is to invoke a competing concerted reaction that gives all retention in the product. The stepwise portion of the reaction could give either the 3:1 retention as in Figure 6 or give the 1:1 ratio shown in Figure 5. Isomerization of the starting material via the 1,4-biradical further complicates the reaction. The basic question still remains. Is the presumed metal-centered 1,4-biradical on the path to the cyclopropanes and if so, is it an intermediate or a transition state, and how long does it exist with respect to bond rotation?

In order to ascertain absolutely what the branching ratio was at the start of the reaction, the stereochemistry of the starting material and product were very carefully examined during the first five percent of the reaction. The tetradeuterometallacylce was chosen for this series of experiments because of its simple proton spectra and the sensitivity of proton NMR spectroscopy. Each spectrum was acquired over a 90 minute period. Despite the long accumulation time, sensitivity was not adequate for determination of the stereochemical ratio of the cyclopropane formed in the first 1%-3% of the reaction. In order to improve the signal-to-noise ratio, difference spectra were employed. Four spectra were acquired. The first spectrum was acquired prior to any photolysis. The first spectrum

was then subtracted from each subsequent spectrum, and a drift correction of the baseline was applied. This dramatically improved the quality of the spectra. The subtraction process removed instrumental artifacts as well as extraneous signals. The spectra and the data from the spectra are shown in Figure 11. These data indicate that the contribution from a concerted reaction must be fairly small, since the cyclopropane formed early in the reaction is still only approximately 6:1 in favor of retention. Examination of the early portion of the reaction allows one only to neglect the isomerization of the starting material, provided that it does not isomerize too greatly. If there had been a large element of a concerted reaction, then one would have expected to observe a greater than 6:1 level of retention in the early stages of the reaction.

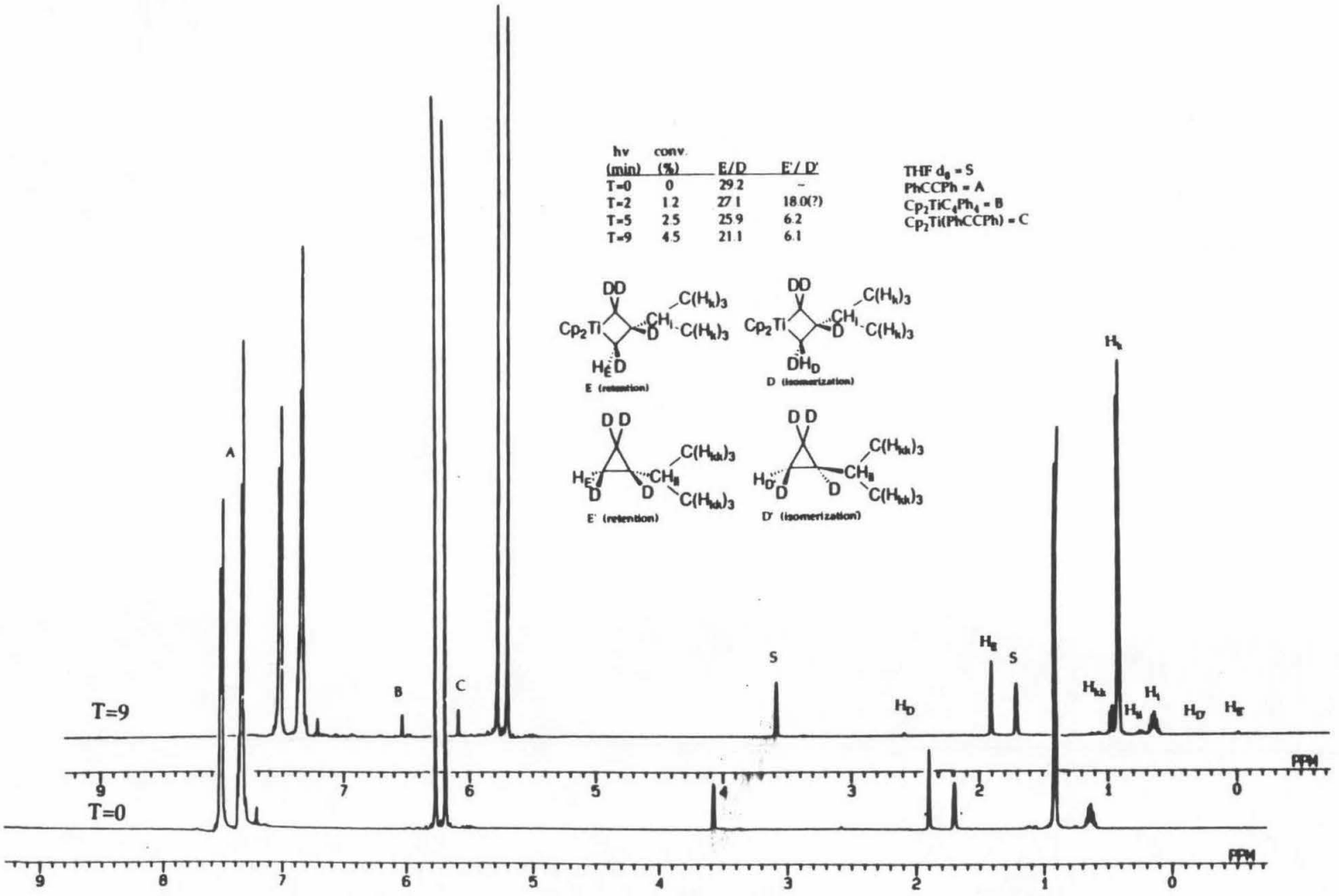


Figure 11. The entire NMR spectrum of the stereochemical experiment used to determine the extent of concerted reaction via examination of the early portion of the reaction.

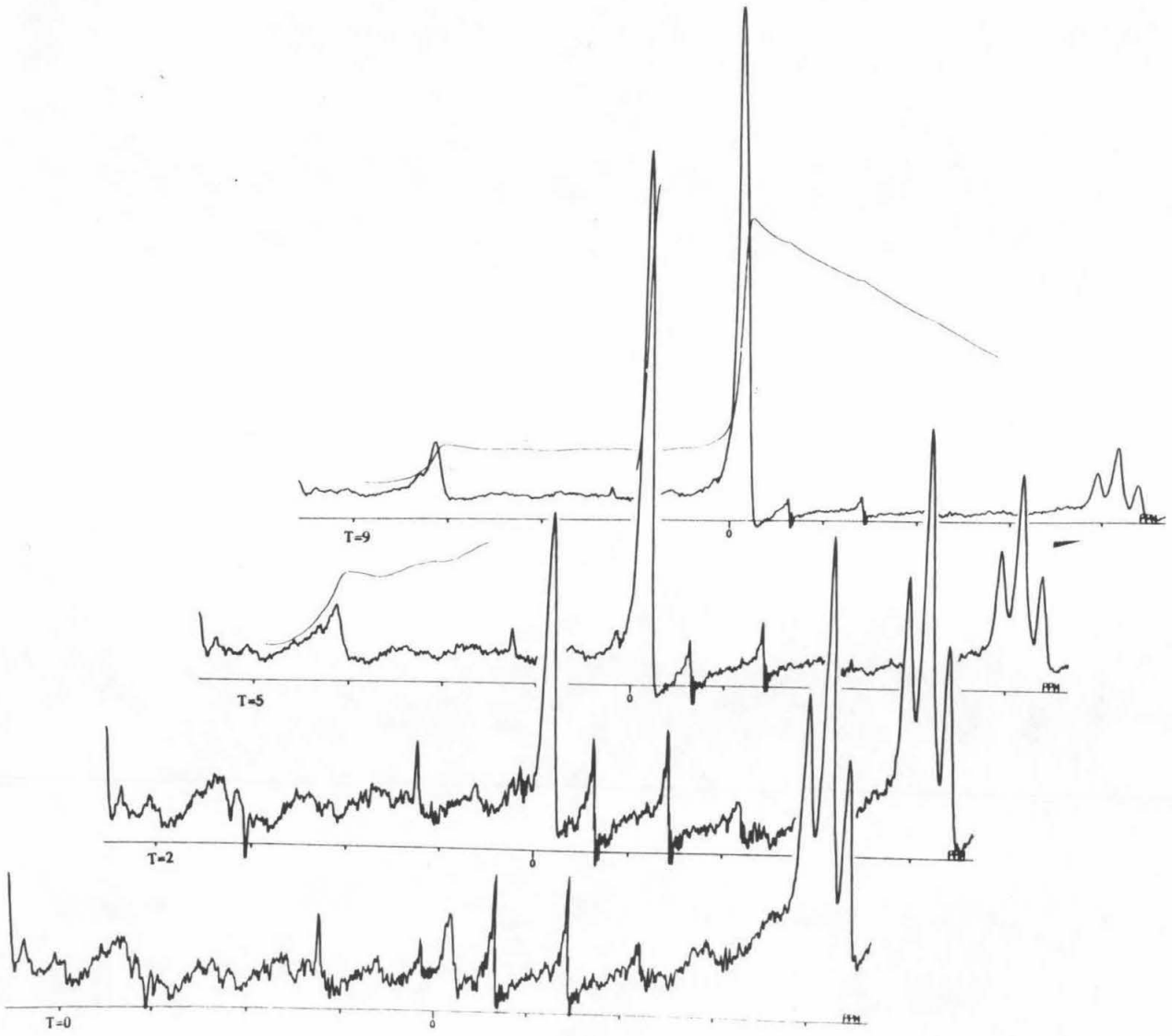


Figure 11. The four spectra prior to subtraction and drift correction.

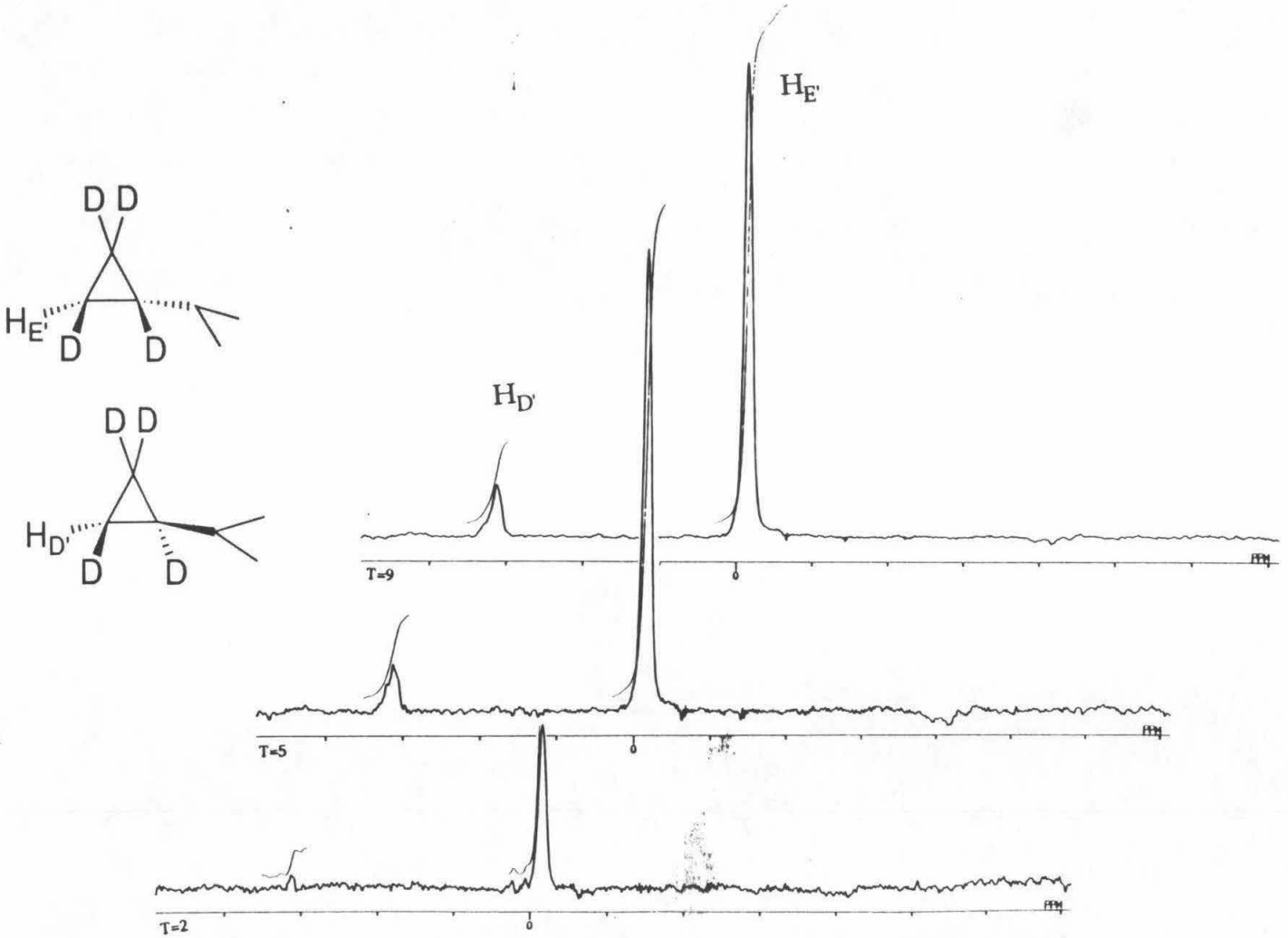


Figure 11. Spectra after subtraction and drift correction.

In order to explain the ~6:1 stereoisomer ratio observed early in all of the photochemical reactions, the possibility of two different simultaneous reaction mechanisms was considered. A competing concerted reaction is needed to explain the extra retention observed in the cyclopropane. The fundamental question concerning this hypothesis is the degree to which this competing reaction is present. The ~6:1 stereoisomer ratio indicates that if the 3:1 branching ratio shown in Figure 6 is in operation in addition to the competing concerted reaction, then the fraction of the molecules undergoing the concerted reaction must be on the order of 50% in order to observe the 6:1 initial branching ratio. If the 1:1 branching ratio for the stepwise reaction were occurring, then the concerted reaction would have to be responsible for >80% of the reaction. Both of these mechanisms, the 50% concerted and 3:1 branched or the 80% concerted and the 1:1 branched, give a fair approximation of the final isomer ratio (3:1) when they are extrapolated to the end of the reaction. However, if such large elements of a concerted reaction were occurring, then the results of the radical clock experiments would be anomalous. The radical clock results are addressed in the following paragraphs.

An elegant method to determine the likelihood of a competing concerted reaction was devised. After the initial observation of the photochemical reductive elimination of cyclopropanes from ß-substituted titanacyclobutanes, bicyclic titanacyclobutanes were investigated. One of the first bicyclic metallacycles to be investigated was the one derived from titanocene methylidene and 3,3-dimethylcyclopropene. Photolysis of this metallacycle in the presence of diphenylacetylene gave the trisubstituted metallacyclobutene shown in Figure 12a. This product was presumed to be

a result of the trapping of the titanium alkylidene by a 2+2 addition reaction with the acetylene.

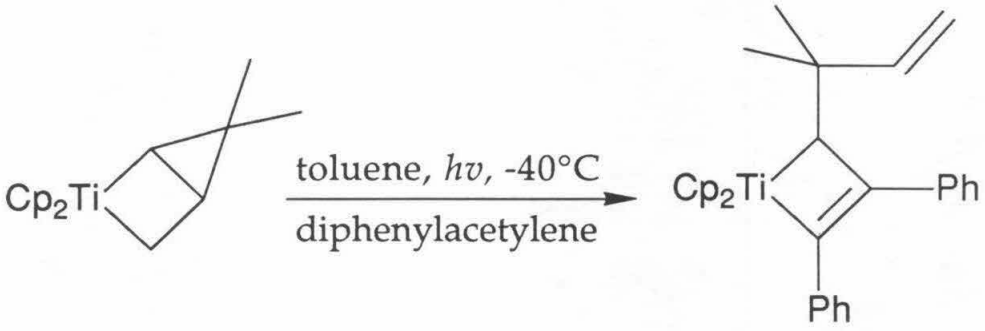


Figure 12a. Trapping of the titanium alkylidene by diphenylacetylene.

The alkylidene could be observed directly either as the trimethyl phosphine adduct by photolysis in the presence of trimethyl phosphine, or as a THF adduct by photolysis of the titanacycle at -78 °C in THF. Many synthetically useful applications of this reaction have been found. The mechanism of the formation of the alkylidene was rationalized to be the result of cyclopropyl carbinyl rearrangement.[20] The rearrangement is shown in Figure 12b. The rearrangement is likely to be much faster than a typical cyclopropyl carbinyl rearrangement, since the final product can be drawn in closed-shell form. The exclusive cleavage of the unsubstituted bond is believed to result since this bond is weaker than the other bond and since unsubstiuted carbon forms a stabilized radical.[21] Also it is important to note the complete absence of any product associated with reductive elimination. Neither bicyclobutane nor 4-methyl-1,3-pentadiene (some transition metals are known to rearrange bicyclobutanes to butadienes) was observed. Reductive elimination followed by edge attack on the 2,2-

dimethylbicyclobutane cannot be ruled out. However, at temperatures as low as -78 °C, the only product observed is the titanocene alkylidene.

Figure 12 also shows how the titanium alkylidene can trap itself in a 2+2 reaction to regenerate the starting bicyclic metallacycle in 95% yield. The kinetics of this self-trapping reaction was investigated in THF by following both the rate of appearance of the β proton in the titanacycle and by following the rate of disappearance of the alkylidene proton at 12.5 ppm. The reaction was unimolecular. The alkylidene phosphine adduct did not undergo this self-trapping reaction. The kinetic parameters of the closure as derived from an Eyring plot are $\Delta H^{\ddagger}$=17.6±0.7 kcal/mole and $\Delta S^{\ddagger}$=4.1±0.5 eu at 230.15 K. Repeating the photolysis at -78 °C in either toluene or diethyl ether resulted in decomposition of the alkylidene. Preliminary NMR evidence suggests that the alkylidene can be stabilized by olefins such as isobutylene without forming a metallacycle. This observation could have implications for understanding the mechansim of metallacycle formation, since it seems to imply that an olefin alkylidene adduct lies on the reaction pathway to metallacycle formation.

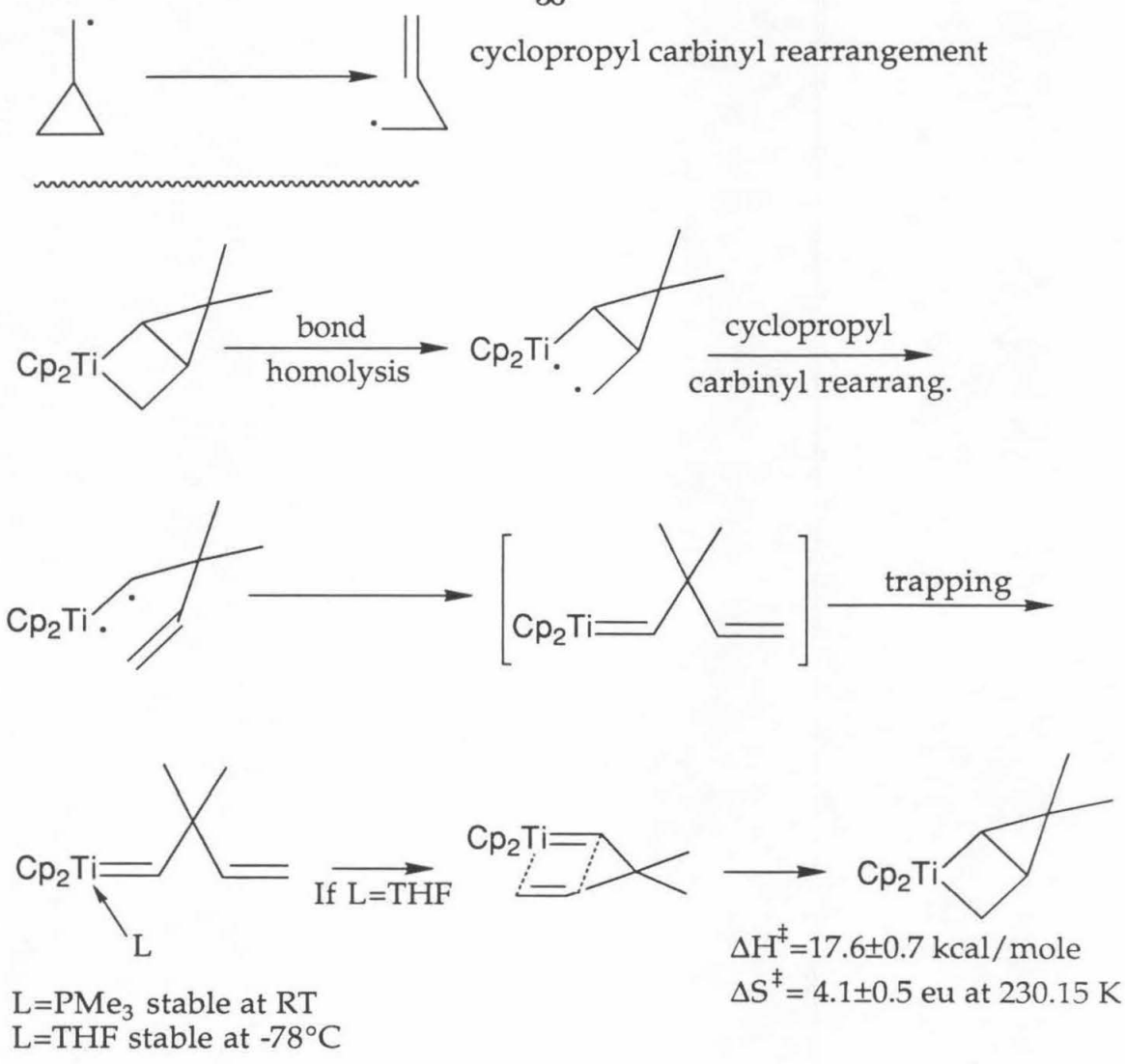


Figure 12b. Radical trapping of 1,4-biradical and subsequent self-trappng.

In order to determine whether or not the absence of any bicyclobutane from the photolysis of the dimethylcyclopropene metallacycle was a result of a genuine cyclopropyl carbinyl rearrangement, a series of bicyclic titanacyclobutanes was synthesized and investigated. The first two metallacycles studied were derived from cyclopentene and from

norbornene. Upon photolysis both metallacycles underwent reductive elimination, yielding [3.1.0]tricyclohexane and cyclopropylnorbornene respectively.[22] However, along with each of these products was another product. The exact yields were not determined because of the inefficiency of the photolysis and the low yield of the side products. The other product was 1-methylcyclopentene and 2-methylnorbornene, respectively. The exact origin of these products is unclear at this time. The bicyclic titanacyclobutanes, with the exception of the one derived from 3,3-dimethylcyclopropene, have quantum yields much lower than those of the parent β-substituted titanacycles. This low quantum yield translates into longer photolysis. Long photolysis generates radicals from secondary photochemistry of the primary photoproducts.[23] Labelling studies from gem-α,α-dideutero cyclopentene-derived titanacycle (synthesized from cyclopentene and source of deuterated titanocene methylidene) show that >90% of the deuterium ends up in the methyl group of the 1-methylcyclopentene. Collectively, these results indicated that photochemical reductive elimination is possible from bicyclic titanacyclobutanes, but it does not address the effect of ring strain on the reaction shown in Figure 12. Bicyclobutanes are strained relative to the starting material. The bicyclic metallacycles investigated are illustrated in Figure 13.

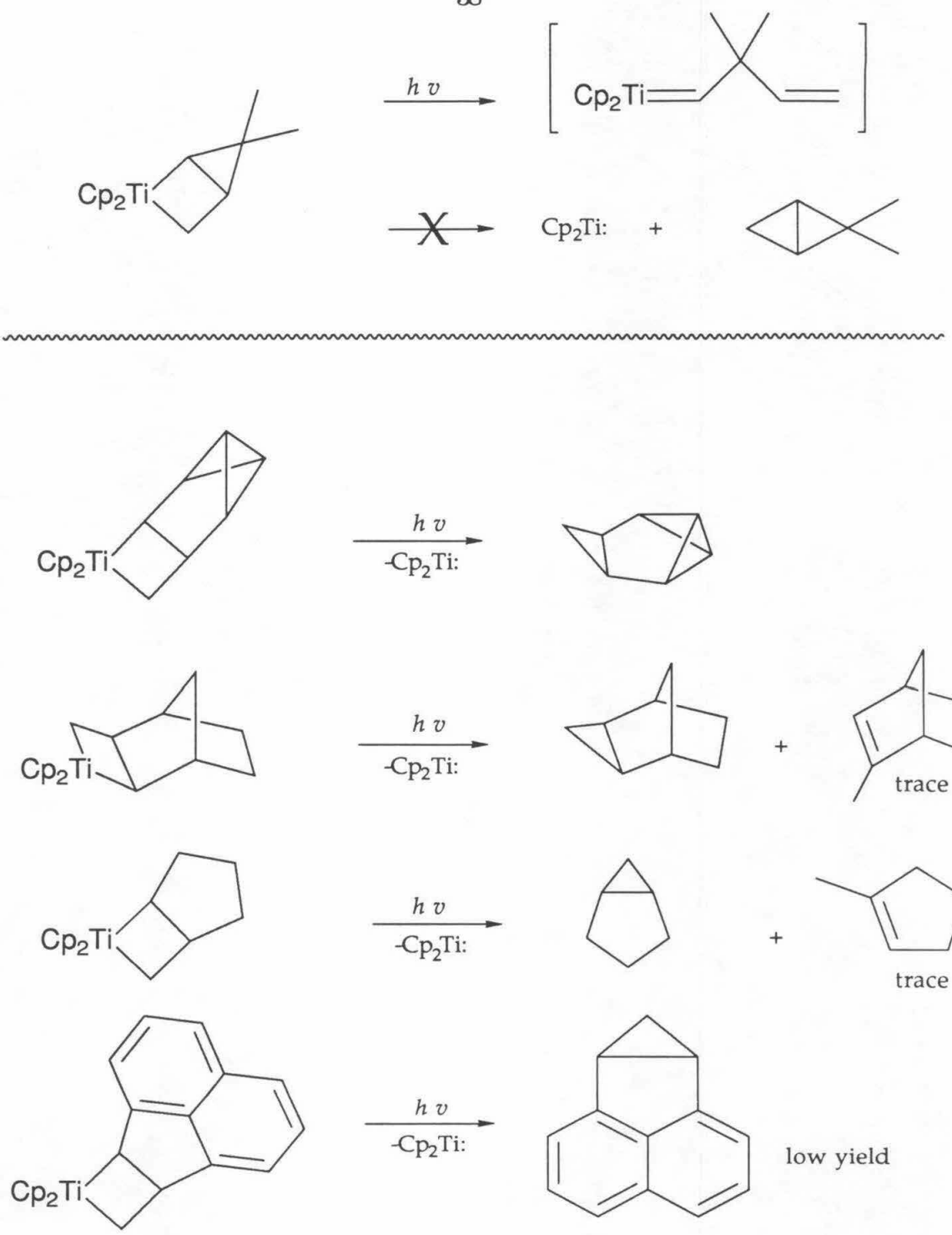


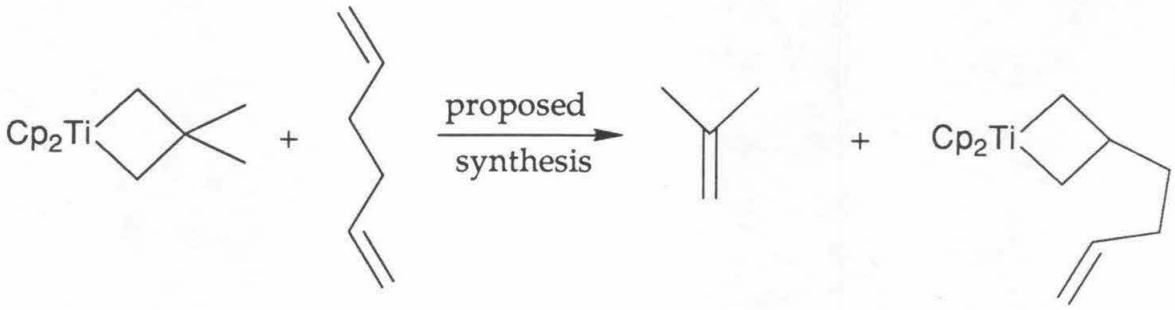
Figure 13. Ring strain does not affect reductive elimination.

The effect of ring strain on the reaction shown in Figure 12 was addressed through the investigation of highly strained metallacycles. The metallacycle derived from benzvalene and titanocene methylidene was synthesized and photolyzed. It was found to undergo reductive elimination to only one product which from literature spectra, ^{13}C NMR, ^{1}H NMR, and ^{1}H-^{1}H correlated spectroscopy (COSY), was identified as cyclopropylbenzvalene.[24] Literature values give the difference in strain energy between cyclopropane and bicyclobutane as ~37 kcal/mole.[25] Calculations by MM2 show that benzvalane (hydrogenated benzvalene) has a strain energy of ~74 kcal/mole, and the cyclopropanated benzvalene product has a strain energy of 124.4 kcal/mole. The difference is ~50 kcal/mole. This energy change is much greater than the change that would be associated with the generation of gem dimethylbicyclobutane from the cyclopropene-derived metallacycle. Therefore, strain energy cannot be the reason that this metallacycle fails to undergo reductive elimination. These results are summarized in Figure 13. The yield of the reaction generating cyclopropylbenzvalene was not optimized as the material had a tendency to decompose spontaneously. In some of the reactions, traces of methylbenzvalene may have been observed.[26] The lack of an effect of ring strain on the reductive elimination implies that the rearrangement of the dimethylcyclopropene-derived titanacycle illustrated in Figure 12 is a genuine cyclopropyl-carbinyl rearrangement.

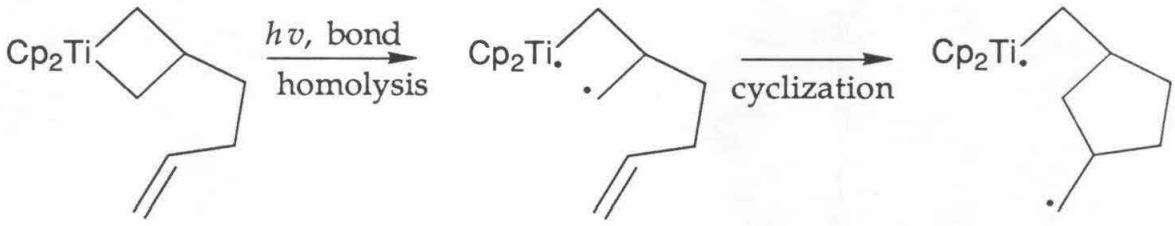
If the element of concerted reaction is as great as indicated by the labelling studies, on the order of 50% or 80%, significant amounts of bicyclobutanes should have been observed. Even in glass solvents at 77 K bicyclobutane was not observed.[27] An additional observation concerning the photochemistry of the cyclopropene-derived metallacycle concerns

quantum yield. The cyclopropene-derived metallacycle has a quantum yield that is qualitatively between 2 and 10 times that of the ß-*tert*-butyl metallacycle. This observation is consistent with rapid trapping of the 1,4-biradical. The recombination of the 1,4-biradical is less likely since rapid rearrangement is possible. The exact measurement of the quantum yield is complicated by the thermochromic nature of the two different titanacycles and by the fact that each generates a different, intensely colored photoproduct. However, side-by-side photolysis of the cyclopropene titanacycle and the β-*tert*-butyltitanacyclobutane shows that in the early stages of the reaction, there is at least twice as great a quantum yield for the cyclopropene metallacycle. The yields seem to be a function of the nature of the efficiency of the trap.

After the initial success of the cyclopropene-derived radical trap, attempts were undertaken to synthesize other radical traps that would confirm the results of the cyclopropene metallacycle. Two different radical traps were envisioned. The first was based on a 5-exo-trig cyclization. The starting titanacyclobutane and the envisioned rearrangement are shown in Figure 14. While the synthetic route to this molecule was conceptually straightforward, the product proved to be unstable. Reaction of the metallacycle derived from isobutylene and 1,5-hexadiene in perdeuterobenzene revealed that at least 3 major products were formed none of which were thermally stable. It is believed that ß-elimination from the presumed product was the major problem. No attempts were made to remedy this problem by additional substitutions in the beta position.



Possible Trapping Reaction



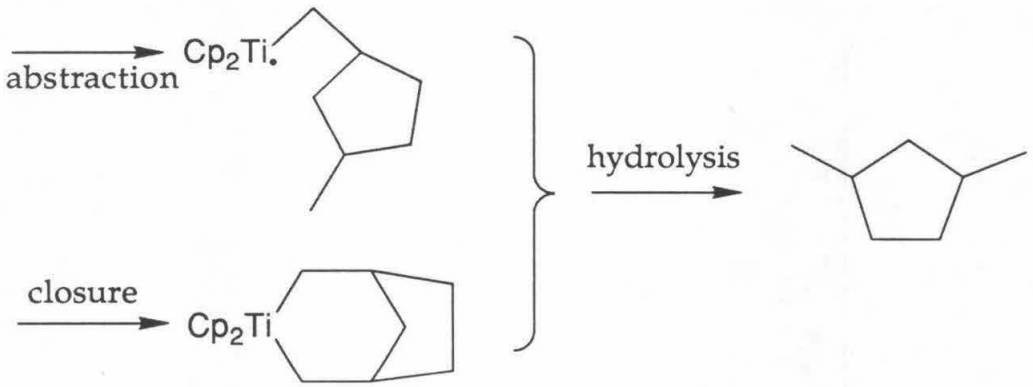
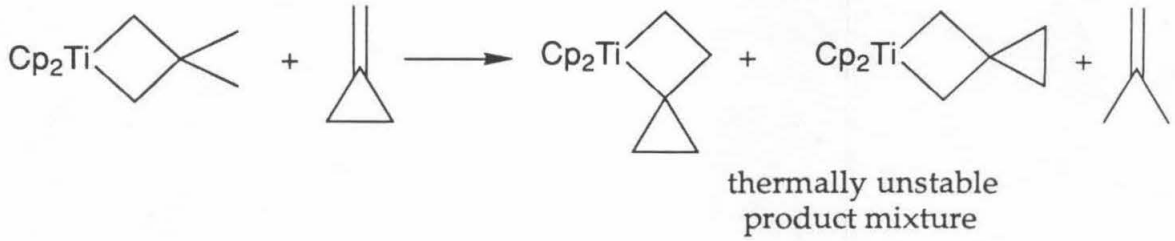


Figure 14. An unsuccessful attempt at radical trapping.



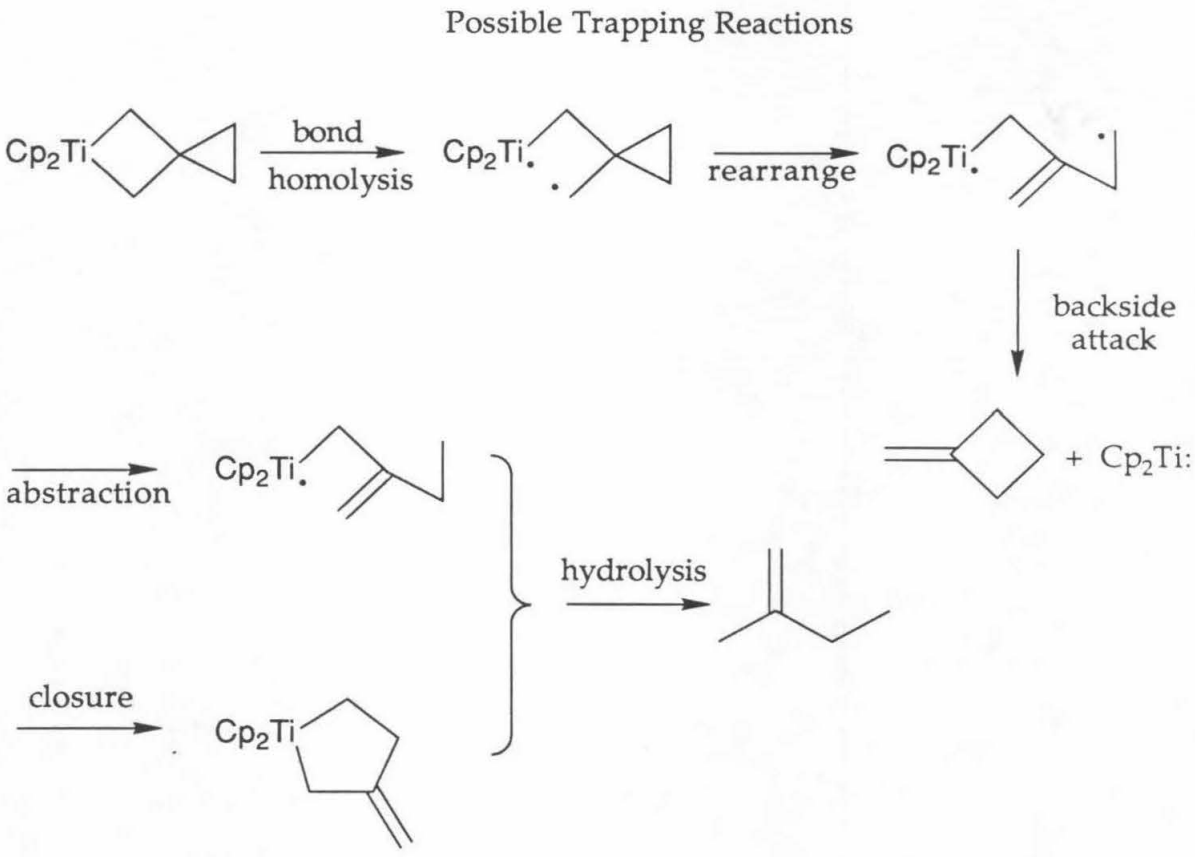
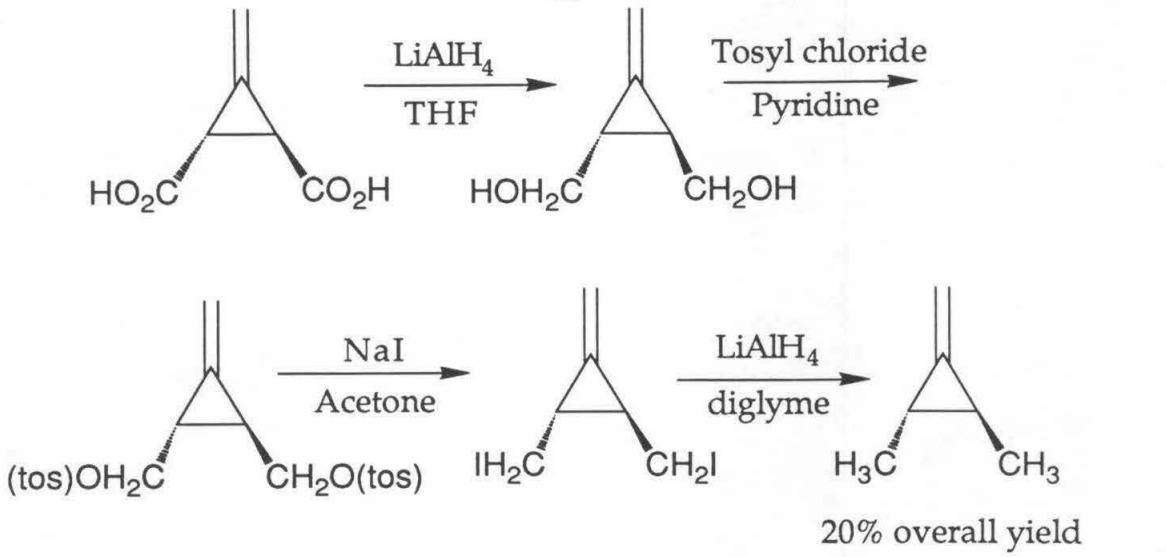


Figure 15. Alternative attempts at radical clocks.

The next attempted radical clock was extremely attractive since it would provide a symmetrical starting material. The proposed starting material and its possible rearrangements are shown in Figure 15.

Reaction of methylenecyclopropane with a titanium methylidene source such as β,β-dimethyltitanacyclobutane resulted in two major products. They were tentatively identified as the α and β spiro metallacycles shown at the top of Figure 15. The material proved to be surprisingly thermally sensitive, decomposing above ~0 °C. In order to circumvent the mixture of products the bulkier trans-2,3-dimethylmethylenecyclopropane was synthesized, Figure 15a, and was allowed to react with the isobutylene metallacycle. Surprisingly, it failed to prevent formation of the α spirometallacycle and gave additional undetermined products. The extreme thermal instability of the product combined with the inefficiency of the reaction made isolation of pure material from a scaled-up reaction unattractive. Additional attempts along this line were not pursued.



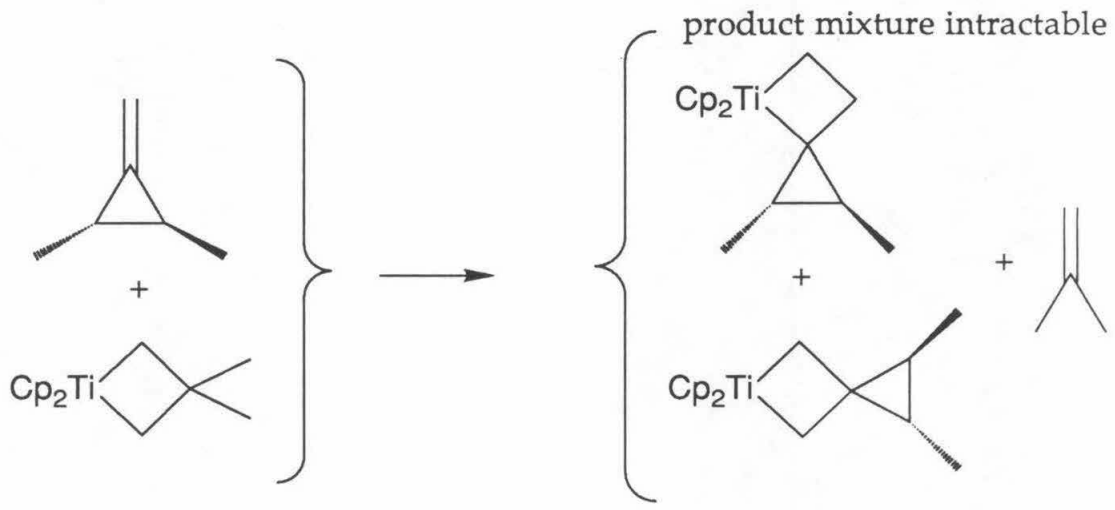


Figure 15a. Attempted synthesis of spirometallacycle using steric bulk to control substituent stereochemistry.

Trapping studies were undertaken to more learn more about the 1,4-biradical that presumably is generated from the photolysis of titanacyclobutanes. It has been observed that for other titanocene alkyls,

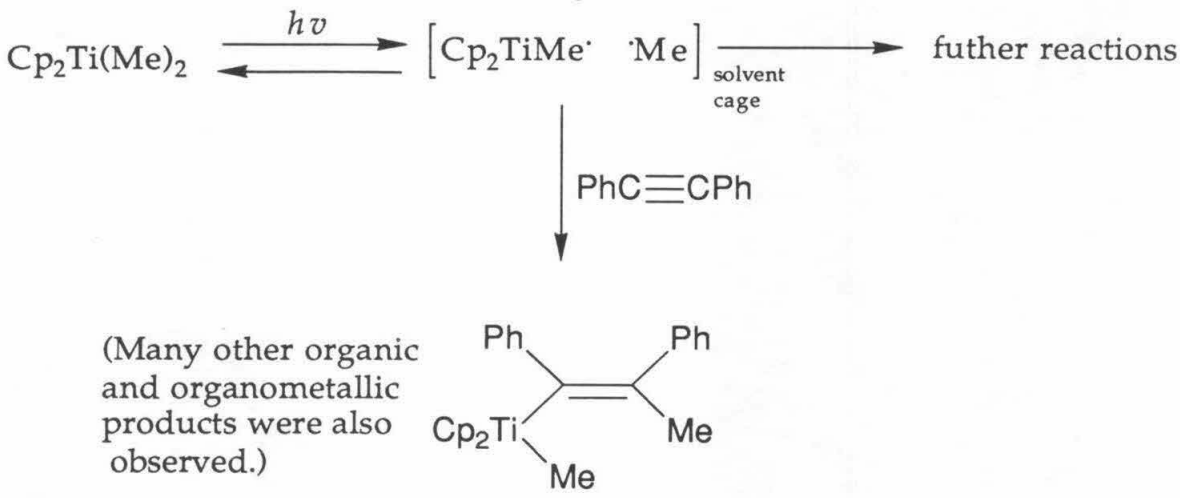


Figure 16. Intermolecular trapping of a radical pair.

photolysis in the presence of the appropriate trap can yield products derived from interception of the geminate radical pair that is formed.[28] An example is shown in Figure 16. This trapping is relatively difficult since the geminate radical pairs are extremely short-lived.[29] Photolysis of the β-*tert*-butyltitanacyclobutane in neat carbon disulfide, acetonitrile and 2-butyne were performed. Neither reaction provided products that could be ascribed to interception of a 1,4-biradical. The nonvolatile organometallic fraction of each reaction was NMR-inactive and presumably paramagnetic. The results of the reactions were inconclusive. The α,β-diphenyltitanacyclobutene was photolyzed in neat carbon disulfide in order to trap the potential biradical. Again, only paramagnetic products were produced, precluding further examinations along these lines. Photolysis of a THF glass containing 2-butyne and a metallacycle produced, upon photolysis at 77 K and subsequent annealing, only the expected tetramethyltitanocenecyclopentadiene in 90% yield. Products that could be ascribed to interception of the 1,4-biradical could not be observed. Failure to

trap the biradical was not altogether unexpected. If the biradical lifetime is only on the order of a bond rotation as indicated by labelling studies, then intermolecular reaction is unlikely. For dimethyl titanocene only the most efficient of radical traps were found to intercept the geminate radical pair.[30] Presumably, the change from a titanocene dialkyl to a titanacyclobutane changes the geminate radical pair to a 1,4-biradical that is even shorter lived. The metal-centered 1,4-biradical can then be thought of as an extremely efficient self-trapping agent. This is consistent with the results of the stereochemical labelling studies.

As was alluded to earlier, the stereochemistry was examined in a variety of solvents. Besides investigations in THF and toluene, the stereochemistry was examined in carbon disulfide and acetonitrile. The dielectric constant of acetonitrile is very different from that of THF and toluene, which are fairly similar.[31] The results in carbon disulfide were complicated since the reaction mixture became paramagnetic upon photolysis. The volatiles were removed from the reaction and examined. The volatiles revealed that the ratio of cyclopropane with retention of stereochemistry to that with isomerized stereochemistry was 7:1. Unfortunately, it was impossible to determine the extent of reaction. If the photolysis were stopped early in the reaction, then this result would be consistent. If it were stopped late in the reaction, then the amount of retention would be very high, compared to the 3:1 observed previously in other solvents at the end of the photolysis. This high retention ratio might imply interception of some of the 1,4 biradical prior to isomerization. The intractibilty of the reaction precluded further investigation. The stereochemical studies in acetonitrile were more successful. Photolysis of titanacyclobutanes in acetonitrile produced a black paramagnetic

precipitate independent of the nature of the trap. However, it did not interfere with the examination of the reaction by NMR. The initial cyclopropane was formed with slightly more retention, 7.9:1 than that in toluene or THF. However, this number was close to the error bounds for the integration of the stereochemical studies in THF and toluene. The final stereochemical ratio was 3:1, identical with other results. This result argues against zwitterionic or charge-separated species on the reaction pathway. It would be expected that changing the solvent polarity so much would affect the stereochemical results if charge-separated species were present.

The stereochemistry was also investigated in glass solvents. The reactions were complicated by the fact that typical glass solvents are not commerically available as their perdeuterated analogues. Again, deuterium NMR was employed jointly with proton NMR. The tetradeutero metallacycle in 2-methyl-THF was photolyzed at 77 K. Integration of the cyclopentadienyl resonances of the starting stereolabelled titanacyclobutane and titanacyclopentadiene (diphenylacetylene was included in the reaction mixture for the purpose of providing a tractable product) after warming indicated that the extent of reaction was 81%. The cyclopropane formed indicated 6.5:1 retention to isomerization. This is approximately twice the ratio that would be expected if the reaction were carried out at -20 °C. The volatiles were removed from the reaction mixture and reanalyzed by NMR. The stereochemistry of the cyclopropanes in this volatile fraction indicated a 7.8:1 retention:isomerization stereo-ratio. This number was within the error bounds of the earlier number. Photolysis in a glass was repeated in the same manner in perdeutero toluene. Toluene forms a cracked glass at 77 K. Examination of the reaction after warming indicated the extent of

reaction to be 16%. The cyclopropane stereochemistry was found to be 8.9:1. Again, more retention was found when the photolysis was carried out at 77 K than when the photolysis was carried out at -20 °C. In order to confirm these results, the reaction was repeated in 2-methyltetrahydofuran, and the stereochemistry was determined by deuterium NMR. The results were not unequivocal due to the difficulties in deuterium NMR with these compounds; small resonances are easily lost in the noise or swamped out by larger signals, but more retention was evident than if the reaction had been performed at -20 °C. These results could be rationalized by a number of factors. For example, at 77 K in a glass, bond rotation could be hindered by the matrix and temperature. There could be a low-temperature differentiation of a singlet and triplet pathway. Attempts were undertaken to address the temperature effects by photolyzing a labelled metallacycle in benzene at -78 °C. The solvent did not allow much light to penetrate the sample. This translated into overphotolyzing the surface of the reaction mixture (overphotolysis seems to result in metal-cyclopentadiene bond homolysis) and complicated the subsequent NMR analysis. While the stereochemical results of the glass photolysis did not clarify the reaction mechanism, they did indicate that the reaction does not involve a large degree of rearrangement. The matrix studies also demonstrate that the reaction is probably unimolecular.

Other attempts to delineate the reaction more clearly failed. For example, no new ESR signals were observed when a sample of a metallacycle in a 2-methyltetrahydrofuran glass was irradiated in the cavity of an ESR spectrometer at both 8 K and 77 K. Only a weak broad line was observed, both prior to and during photolysis. The signal was attributed to trace titanium(III) impurities.

The thermal chemistry of titanacyclobutanes is characterized by an allowed 2+2 addition. Organic $\pi 2s + \pi 2s$ reactions are orbitally forbidden. It is fairly clear that photolysis of titanacyclobutanes yields a 1,4-biradical. Organic 1,4-biradicals are a well-known species. They can be generated from diazo compounds and from photochemical 2+2 cycloadditions. Organic 1,4-biradicals do not generate cyclopropane and carbene. The photochemistry of titanacyclobutanes does not yield olefin and titanium methylidene (the expected products of retro 2+2 cleavage). Instead, photolysis induces reductive elimination of cyclopropane. This is very surprising since it is uphill thermodynamically from both the starting material and the 2+2 products. A summation of the chemistry is shown in Figure 17.

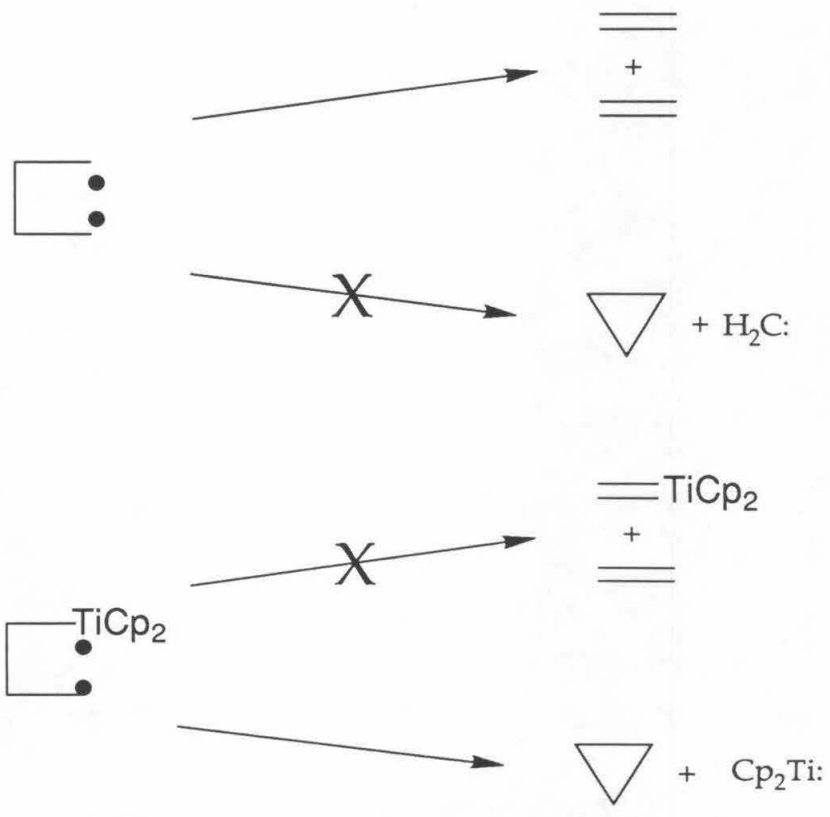


Figure 17. Comparison of organic and inorganic 1,4-biradicals.

While the mechanism of the photochemical reductive elimination is not entirely understood and many of the conclusions rest on admittedly tenuous ground, a working hypothesis of the reaction has emerged. The metallacycle undergoes photolysis to generate a metal-centered 1,4-biradical. The lifetime of this biradical is on the order of a bond rotation. This biradical either recombines or reductively eliminates cyclopropanes. Evidence suggests that there is no competing, concerted reaction. The likelihood of reforming is approximately the same as for reductive elimination. The time required for the bond rotation in the wedge of the metallacycle may be longer than that of a free carbon-carbon bond. Additionally, the remaining orbital on the titanocene fragment may somehow stabilize the carbon-centered radical and thus slow carbon-carbon bond rotation. This "stabilization" may also direct the attack of the radical towards the other metal carbon bond.

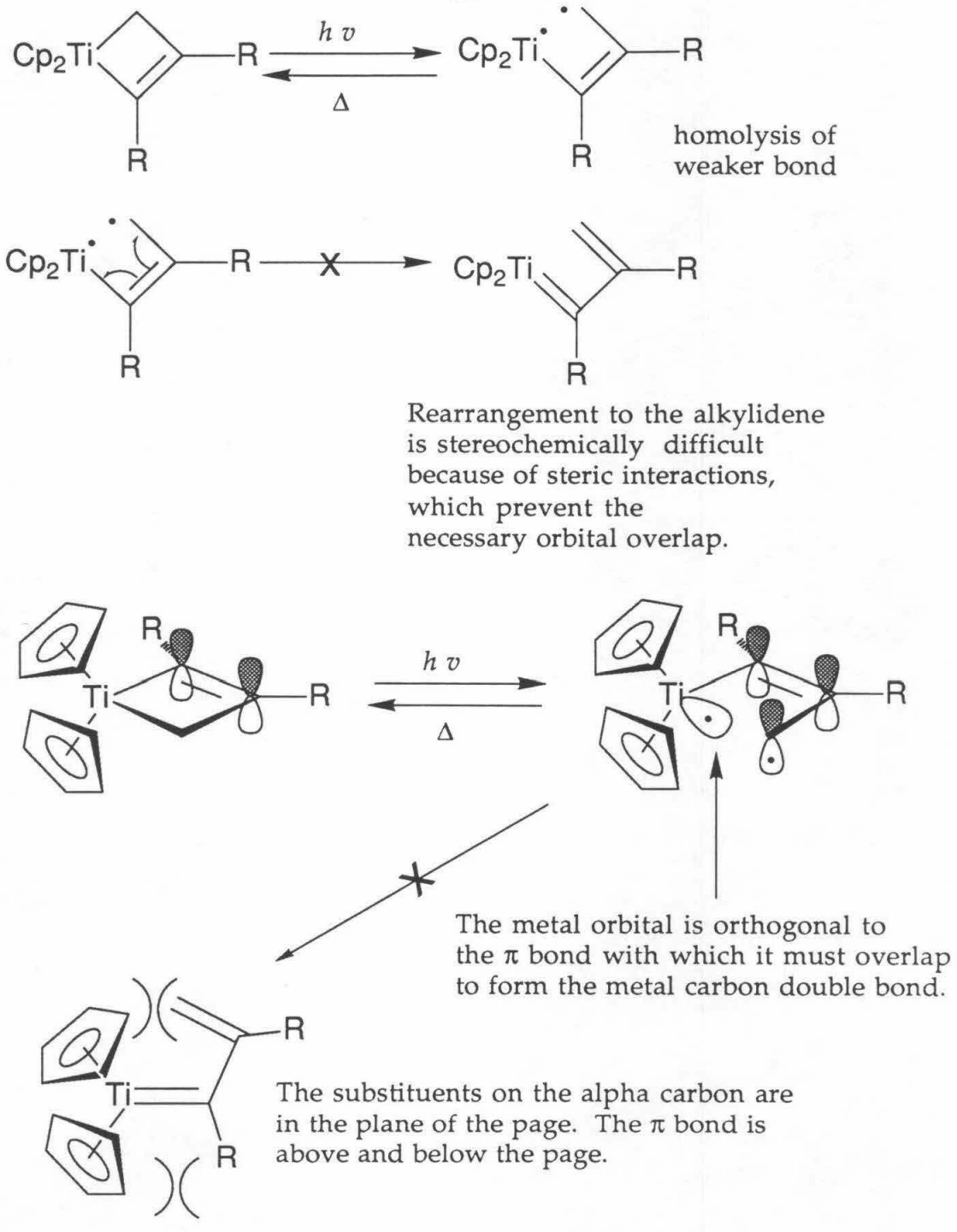


Figure 18. Photochemical inertness of titanacyclobutenes is still consistent with a 1,4-biradical.

One of the measures of the quality of a hypothesis is its utility in predicting other results. The short-lived 1,4-biradical is useful for explaining the lack of photochemical reactivity of bis(η^5-cyclopentadienyl)titanacyclobutenes. The titanacyclobutenes are extremely photochemically inert, remaining unchanged after 24 hours of photolysis. If a 1,4-biradical were formed, possibly it could be expected to rearrange rapidly to the vinyl titanium alkylidene shown in Figure 18. The failure to rearrange results from stereoelectronic factors. In order to rearrange as shown in Figure 18, the titanium carbon bond must rotate 90° to overlap the π bond and the metal orbitals. This rotation is prevented by the cyclopentadiene rings, which form a sandwhich over the metal orbitals. The compatability of the above hypothesis with other results is particularly rewarding.

Experimental Section:

General Procedures. All work involving air- and/or moisture-sensitive compounds was performed using standard high-vacuum or Schlenk-line techniques under argon purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Work involving manipulation of air-sensitive compounds was performed inside a drybox under nitrogen in a Vacuum Atmospheres dry box equipped with a -40 °C refrigerator and a dry-cool recirculator. Proton, deuterium, and carbon NMR spectra were recorded on a JEOL FX-90Q (89.9 MHz ^{1}H, 22.5 MHz, ^{13}C), and a JEOL GX-400 (399.65 MHz ^{1}H, 61.35 MHz ^{2}H, 100.67 MHz ^{13}C), on a Varian EM-390 (90 MHz ^{1}H), and on a Varian XL-200 (200 MHz ^{1}H). Proton chemical shifts are referenced to internal residual protiosolvents. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Deuterium chemical shifts are referenced to natural abundance deuterium in the solvent. UV-vis spectroscopy was performed with a Hewlett-Packard 8154A diode array spectrophotometer. Gas chromatography analyses (VPC) were performed on a Shimadzu GC-Mini-2 flame-ionization instrument with a 50 meter capillary column and a Hewlett-Packard model 339A integrator. Preparative VPC was performed on a Varian 920 Aerograph with a thermal conductivity detector equipped with a Hewlett Packard 7127A strip recorder (columns: 6 ft by 1/4 in, SE-30 or 4 ft by 1/2in, silver nitrate). Thin-layer chromatography (TLC) was performed on precoated TLC plates (silica gel 60 F-254, EM Reagents). Flash chromatography was by the method of Still et al.[32], using silica gel 60 (230-400 mesh ATMk, EM Reagents). Elemental analysis was performed at the analytical facilities of the California Institute of Technology or at

Galbraith Labs. Photolysis was performed with a 450 watt high pressure mercury Hanovia lamp. Temperatures were maintained with clear pyrex dewars filled with isopropanol at the desired temperature. Temperatures cited reflect the final temperature the bath reached at the end of photolysis; typically a change of only 10 degrees was observed. All photolyses were Pyrex-filtered unless otherwise stated.

Materials. The solvents were purified as follows: Toluene, benzene, tetrahydrofuran, and diethyl ether were distilled under vacuum from sodium benzophenone ketyl into solvent flasks equipped with Teflon screw-type valves. Methylene chloride, acetonitrile, chloroform, and pyridine were distilled from calcium hydride at atmospheric pressure and subsequently freeze-pump-thaw degassed. Dimethylsulfoxide was distilled from calcium hydride at reduced pressure. Carbon disulfide was distilled from phosphorus pentoxide. Diphenylacetylene was recrystallized from toluene. All volatile acetylenes were distilled and degassed prior to use. Solvents used in photochemical reactions (typically, THF, benzene, toluene, and 2-methyltetrahydrofuran) were vacuum-distilled directly into the reaction vessels (after predrying over sodium) from sodium-potassium alloy and were thoroughly degassed prior to use. Titanacyclobutanes derived from isobutylene,[33] neohexene[34], norbornene[35] 2,2-dimethylcyclopropene[36] were synthesized according to literature procedures. Methylene cyclopropane, 2,2-dimethylcyclopropene and 2,2,3,3-tetramethylcyclobutene were received as gifts from Scott Virgil. The metallacyclobutane derived from titanium methylidene and benvalene was supplied by Tim Swager. Literature procedures were used to synthesize trans-2,3-dimethylmethylenecyclopropane.[37] β-dimethylsilyl-titanacyclobutane and

β-dimethylsilylzirconacyclobutane were synthesized from adaptations of the literature procedures.[38]

Perdeuterodimethylmercury: A 300 mL three-necked flask was equipped with a condenser, addition funnel, and septum. The apparatus was charged with 6.44 g of magnesium metal turnings (0.265 moles) and subsequently flame-dried under vacuum, and back-filled with argon. Approximately 1 mg of iodine was added and heated to sublimation under an argon purge and swept out of the flask. The addition funnel was charged with 34.91 grams of perdeuteroiodomethane (0.241 moles previously distilled from phosphorus pentoxide and stored over copper wire). Onto the magnesium was cannulated 15 mLs of diethyl ether. Approximately 5 mLs of the halide was added quickly to the ether/magnesium. After the reaction initiated, as evidenced by an exotherm, the remainder of the halide was added at such a rate as to maintain gentle reflux. The reaction mixture was stirred 8 hrs. Under an argon purge, 32.69 g of mercuric chloride (0.120 moles) was slowly and carefully added down the condenser. The reaction mixture was then refluxed for 24 hours. The reaction mixture was allowed to cool and was then quenched with water and filtered. Aqueous workup followed by distillation of the solvent and finally the product, 86-93 °C, afforded 13.5 g $(CD_3)_2Hg$ (57 mmole, 24%).

Perdeuterotrimethylaluminum: A heavy-walled glass ampoule equipped with a Kontes-type valve was equipped with a stir bar and then charged in a drybox with 4.62 g of aluminum powder (0.171 moles). Into the flask was cannulated 13.5 g of perdeuterodimethylmercury (57 mmole). The reaction mixture was freeze-pump-thaw-degassed and then heated to

90 °C for 20 hours. The $Al(CD_3)_3$ was vacuum-distilled from the mercury metal into a sealable U trap to provide 3.00 g of product (37 mmole, 97%).

Tebbe Reagent-d8: In a drybox a small Schlenk flask was charged with 4.10 g of titanocene dichloride (16.46 mmole). To the titanocene dichloride was added 2.95 g of perdeuterotrimethylaluminum (36.4 mmole), followed by 15 mLs of freshly distilled and degassed toluene. The reaction mixture was heated to 55 °C for 39 hours on a Schlenk line. After cooling, 10 mLs of pentane was layered on top, and the mixture was slowly cooled to -20 °C; over the course of 48 hours crystals formed. The crystals were isolated and washed with additional pentane and dried under vacuum at -20 °C. A second crop of crystals was obtained by cooling the mother liquors to -50 °C and isolating them in a similar manner. A third crop of crystals was obtained by removing the solvent from the mother liquors, dissolving them in 10 mLs of toluene and 10 mLs of pentane and slowly cooling the resulting solution to -20 °C. The first crop yielded 1.75 g; the second, 1.21 g, and the third, 1.79 g (4.75 g total, 16.9 mmole, 103%).

Isobutylene-d8: In ~150 mLs of THF was dissolved 40.0 g of triphenylphosphine (0.152 moles). To this solution was then added 25.0 g of trideuteroiodomethane (0.172 moles). After 2 hours at room temperature, the resulting precipitate (59.6 g, 0.143 moles, 96%) was collected by filtration and dried under vacuum. A large Schlenk flask was charged with 25.13 g of the above phosphonium salt (61.7 mmoles) and then taken into the drybox where it was additionally charged with 3.00 g of sodium hydride (0.125 moles). On a Schlenk line approximately 150 mLs of THF was added, after which the reaction mixture was refluxed for 12 hours. The reaction mixture was then filtered through dry celite and then concentrated under vacuum. The phosporane was suspended in 100 mLs of toluene and cooled

to 0 °C. To the cooled suspension was added 3.50 mLs of dry perdeuteroacetone (3.05 g, 47 mmole) by syringe. The reaction mixture was stirred for 3 hours at 0 °C and then for 30 minutes at ambient temperature. The volatiles were vacuum-transferred to a Schlenk flask equipped with a Kontes valve. The isobutylene was distilled from the reaction mixture through a Vigreaux column cooled to 0 °C. The product (2.544 g, 39.7 mmole, 84%) was vacuum-transferred onto 10 mLs of dry, degassed methylene chloride for storage.

α,α,α',α'-tetradeutero-β,β-dimethyl-titanacyclobutane: The second and third crops (3.00 g, 10.27 mmole) of the Tebbe reagent-d8 from above and 1.50 g of N,N-dimethylaminopyridine (12.30 mmole) were loaded into a small Schlenk flask in a drybox. The solids were cooled to -30 °C outside the box on a Schlenk line. The isobutylene-d8/methylene chloride solution from above was cooled to -30 °C and subsequently cannulated onto the solids. This solution was stirred for 30 minutes, during which time it was allowed to warm to -5 °C. This solution was then cannulated into 110 mLs of well-stirred -35 °C pentane. The resulting suspension was quickly filtered and the filtrate was taken to dryness under vacuum at -30 °C. Final drying was achieved by allowing the temperature to rise to 0 °C during the final five minutes of drying. This solid was then recrystallized from toluene at -50 °C to afford 0.652 g (2.52 mmole, 25%) of product. The mother liquors were taken to dryness to afford another 564 mgs of impure product.

1,2-cis-dideutero-3-methyl-1-butene: A large Schlenk was charged with 20.0 g of zirconocene dichloride (68.4 mmole). The zirconocene dichloride was suspended in 200 mLs of THF and into the suspension was cannulated a THF suspension of 0.72 g of lithium aluminum deuteride (17.2 mmole). A white precipitate formed. The suspension was stirred for 24

hours while protected from light. The zirconocene chloride deuteride (10.5 g, 40.5 mmole, 60%) was allowed to settle and was then washed five times with 25 mLs of THF and then with 50 mLs of diethyl ether. The solid was dried under vacuum and then taken into the dry box. A 500 mL Schlenk flask was charged with 10.1 g of powder zirconocene chloride deuteride (39.0 mmole). Onto this solid was cannulated 100 mLs of toluene and 4.2 mLs of 4-methyl-1-butyne (2.8 g, 41.0 mmole). The suspension was stirred in the dark for four hours, during which time all of the solid dissolved to give a green solution. The volatiles were removed under vacuum to afford a green oil. To this was cannulated 50 mLs of cold pentane. The resulting green solids were dried under vacuum to give a bright-yellow solid, which was broken up with a spatula under a purge of argon. This solid was then suspended in 15 mLs of toluene at 0 °C. Into this 0 °C suspension was syringed 0.800 mLs of deuterium oxide (44.0 moles); the reaction mixture was then stirred for 12 hrs at ambient temperature. The volatiles were vacuum-transferred off the white precipitate onto 4Å molecular sieves. Distillation of the reaction mixture through a jacketed Vigreaux column cooled to 20 °C provided 2.152 g of the olefin (29.84 mmole, 77%).

***E*-1-deutero-4-methyl-1-butene** This material was synthesized in a fashion similar to the 1,2-cis-dideutero-3-methyl-1-butene from above, except that zirconocene chloride hydride was used instead of zirconocene chloride deuteride.

α',α'–dideutero-cis-α,β-dideutero-β-isopropyl-bis(η^5-cyclopentadienyl)titanacyclobutane: A small Schlenk flask was loaded in a drybox with 0.510 g α,α,α',α'-tetradeutero-β,β-dimethyl-titanacyclobutane (1.977 mmole). Outside the drybox it was cooled to -35 °C. Into a small Schlenk flask was vacuum transferred 10 mLs of dry, degassed diethyl

ether and 0.3926 g of 1,2-cis-dideutero-3-methyl-1-butene (5.44 mmole). This solution was cooled to -35 °C and was then cannulated onto the metallacycle. The cooling bath was removed and the solution was stirred at room temperature for exactly 30 minutes. The volume of the solution was reduced by half under vacuum. Slow cooling of the solution to -50 °C afforded, after washing and drying, 267 mg of long, red needles of the desired product (1.003 mmole, 51%). NMR examination (toluene-d8) of the product indicated that the ratio of the α protons trans to the β isopropyl group (δ: 2.67 ppm) to the α protons cis to the β isopropyl group (δ: 1.95 ppm) was 23±1 to 1.

Trans-α–deutero-β-isopropyl-bis(η^5-cyclopentadienyl)titanacyclobutane: This metallacyle was synthesized in a manner similar to that reported above. A small Schlenk flask was charged with 0.722 g of β,β–dimethyltitanacyclobutane (derived from titanocene methylidene and isobutylene) (2.91 mmole). To this was added 15 mLs of diethyl ether and 0.5398 g of **E**-1-deutero-4-methyl-1-butene (7.46 mmole) at -78 °C. The reaction mixture was warmed to room temperature and stirred for 30 minutes, after which time the volume of the solution was reduced by half under vacuum. Slow cooling of the reaction mixture to -50 °C provided, after washing and drying, 0.455 g of product (1.73 mmole, 60%).

Trans-α,β-dideutero-β-isopropyl-bis(η^5-cyclopentadienyl)titanacyclobutane: This material was synthesized as above from 1,2-cis-dideutero-3-methyl-1-butene and β,β–dimethyltitanacyclobutane in 56% yield on a 2 mmole scale.

Additional titanacycles derived from acenaphthylene, benzvalene, and 1,1-dimethylallene were synthesized from the reaction of 1 equivalent of

the appropriate olefin and the ß,ß-dimethyltitanacyclobutane followed by recrystallization from diethyl ether.

Titanacyclobutenes: The appropriate acetylene was allowed to react with one equivalent of the ß,ß-dimethyltitanacyclobutane in diethyl ether followed by recrystallization.

Typical NMR experiment. In a drybox the appropriate metallacycle was placed in a sealable, tared NMR tube. Additional solid reagents were introduced at this time. On a high vacuum line the NMR tube was evacuated and the deuterated solvent was condensed into the tube at 77 K. Any volatile reagents were then also condensed into the tube from previously tared, evacuated, dried vessels. The tube was sealed under dynamic vacuum with a torch. Dissolution of the materials was achieved at low temperature. NMR spectra were recorded at low temperature, typically -20 °C, before photolysis and at intervals during photolysis. Control experiments were undertaken to ensure the separation of thermal and photochemical reactions for each metallacycle employed. Addtionally, the volatile components of each reaction were removed and examined by NMR.

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[14]These two substituents were chosen for a number of reasons. First, isopropycyclopropane and *tert*-butylcyclopropane have nonoverlapping cyclopropane NMR resonances for the protons cis and trans to either substituent. Second, the NMR resonances of the titanacycle and the cyclopropane do not overlap. Third, both of these metallacycles are relatively thermally stable with respect to retro 2+2 cleavage.

[15]"Trap" here refers to added reagents that are used to trap the titanocene. Mass balance indicates that the product besides cyclobutane must be titanocene. Untrapped, the very reactive titanocene reacts intramolecularly or with an additional titanocene molecule to form a black paramagnetic solid, which can interfere with the NMR spectra. The chemistry of this photochemically produced titanocene is discussed in detail in subsequent chapters.

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[19]The resonances for cyclopropane ring of isopropylcyclopropane are at ~0.1 and ~0.3 ppm, depending on the solvent. The resonance of the β proton of the β-isopropyl titanacyclobutane is at ~0.0 ppm.

[20]Wilt, J. W. in *Free Radicals*, Vol. 1, Kochi, J. K., ed., Wiley, New York, p. 398.

[21]Cyclopropane is more acidic than other alkanes and is likely to form a stronger bond to the metal than the alternate alkyl chain.

[22]The products were identified by NMR and GC analysis by comparison with authentic samples derived from Simmons-Smith cyclopropanation of the corresponding cycloalkene.

[23]The quantum yields are as much as 10 times lower qualitatively, depending on the nature of the trap. Additionally, CpH-derived products have been observed in the product mixtures. This probably results from homolysis of the metal Cp bond to form a cyclopentadienyl radical, a known reaction.

[24]Christl, M.; Freitag, G.; Brüntrup, G. *Chem. Ber.* **1978**, *111*, 2307.

[25]Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

[26](a)Burger, U.; Gandillon, G. *Tett. Let.* **1979**, 4281. (b)Burger, U.; Gandillon, G.; Mareda, *J. Helv. Chim. Acta.* **1981** *64*, 844.

[27]Photolysis of the dimethylcyclopropene metallacycle in a cracked glass of toluene and perdeuteroacetone followed by annealing to -78 °C and removal of the volatiles indicated that the major product was the Wittig alkylidene-

transfer product. Repeating the reaction at 77 K in a THF/acetone glass resulted in an uninterpretable reaction mixture that contained a large number of products. It is possible that bicyclobutane was present in either reaction mixture but was not identified because of its low concentration and numerous other products.

[28]Rausch, M. D.; Boon, W. H.; Alt, H. G. *J. Organomet. Chem.* **1976**, *141*, 299.

[29]Van Leeuwen, P. W. N. M.; Van Der Heijden, H.; Roobeek, C. F.; Frijns, J. H. G. *J. Organomet. Chem.* **1981**, *209*, 169.

[30]*ibid.*

[31]Solvent (dielectric constant, dipole moment in Debyes): carbon disulfide, (2.64, 0); toluene, (2.44, 0.36); tetrahydrofuran, (7.32, 1.6); and acetonitrile, (36.2, 3.9).

[32]Still, W. C.; Kahn, M.; Mitra, A. L. *J. Org. Chem.* **1978**, *43*, 2923.

[33]Strauss, D. A.; Grubbs, R. H. *Organometallics* **1982,** *1*, 1658.

[34]Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am Chem. Soc.* **1980**, *102*, 6876.

[35]Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1733.

[36]Gilliom, L. R; Grubbs, R. H. *Organometallics* **1986**, *5*, 721.

[37]Gajewski, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 4450.

[38](a)Tikkanen, W. R.; Liu, J. Z.; Egan, J. W.; Petersen, J. L. *Organometallics* **1984**, *3*, 825. (b) Tikkanen, W. R.; Egan, J. W.; Petersen, J. L. *Organometallics* **1984**, *3*, 1646.

CHAPTER 2

Reaction of Photochemically Generated Titanocene with Acetylenes, Olefins, and Dienes

Introduction:

Since the discovery of ferrocene in 1951, almost all of the first-row, transition-metal metallocenes have been synthesized and characterized. One of the few compounds that has not been isolated as a simple metallocene is titanocene, Cp_2Ti. This failure is not due to lack of effort. Rather, it is believed that the extreme reactivity of the complex has precluded its isolation. Titanocene is highly coordinatively unsaturated in addition to having two unpaired electrons in its calculated ground state. In fact, it has been described as an organometallic analogue of organic carbene, $:CH_2$.

The attention that titanocene has received over the past 20 years has not been merely due to the novelty of synthesizing a missing compound in a series. Rather, titanocene, or at least the products resulting from attempts to synthesize titanocene, have been shown to have a rich and varied chemistry. Additionally, titanocene has been invoked in many stoichiometric and catalytic reaction mechanisms involving bis(cyclopentadienyl)titanium-containing species. Notably, these reactions include hydrogenations, dinitrogen reduction, and olefin polymerizations.

Many routes have been undertaken to synthesize titanocene, each of which has met with differing results. In fact, the great diversity of synthetic routes and the corresponding great variation in products has contributed to the controversy associated with the determination of the intrinsic properties of titanocene.

The first attempt to synthesize titanocene was undertaken shortly after, and closely paralleled, the synthesis of ferrocene. Reaction of two equivalents of sodium cyclopentadienide with $Ti(II)Cl_2$ provided a green

air-sensitive diamagnetic solid, which was not well characterized.[1] This material was presumed to be "titanocene." This type of result and inability to characterize the resultant materials typified many but not all subsequent attempts to synthesize titanocene. Some of the many routes to titanocene that have been investigated include the following: reductive dehalogenation of bis(η^5-cyclopentadienyl)titanium dichloride by both chemical and electrochemical means; hydrogenation of dimethyltitanocene; thermolysis and/or photolysis of either dimethyltitanocene or diphenyltitanocene. These routes to titanocene have been extensively reviewed.[2] A brief synopsis of theses routes is shown in Figure 1. The presumed mechanism for one of the reductions is shown in Figure 2. Titanium hydrides are often encountered in the attempted syntheses of titanocene. The mechanism in Figure 2 shows how these hydrides and shifted cyclopentadienyl rings are generated.

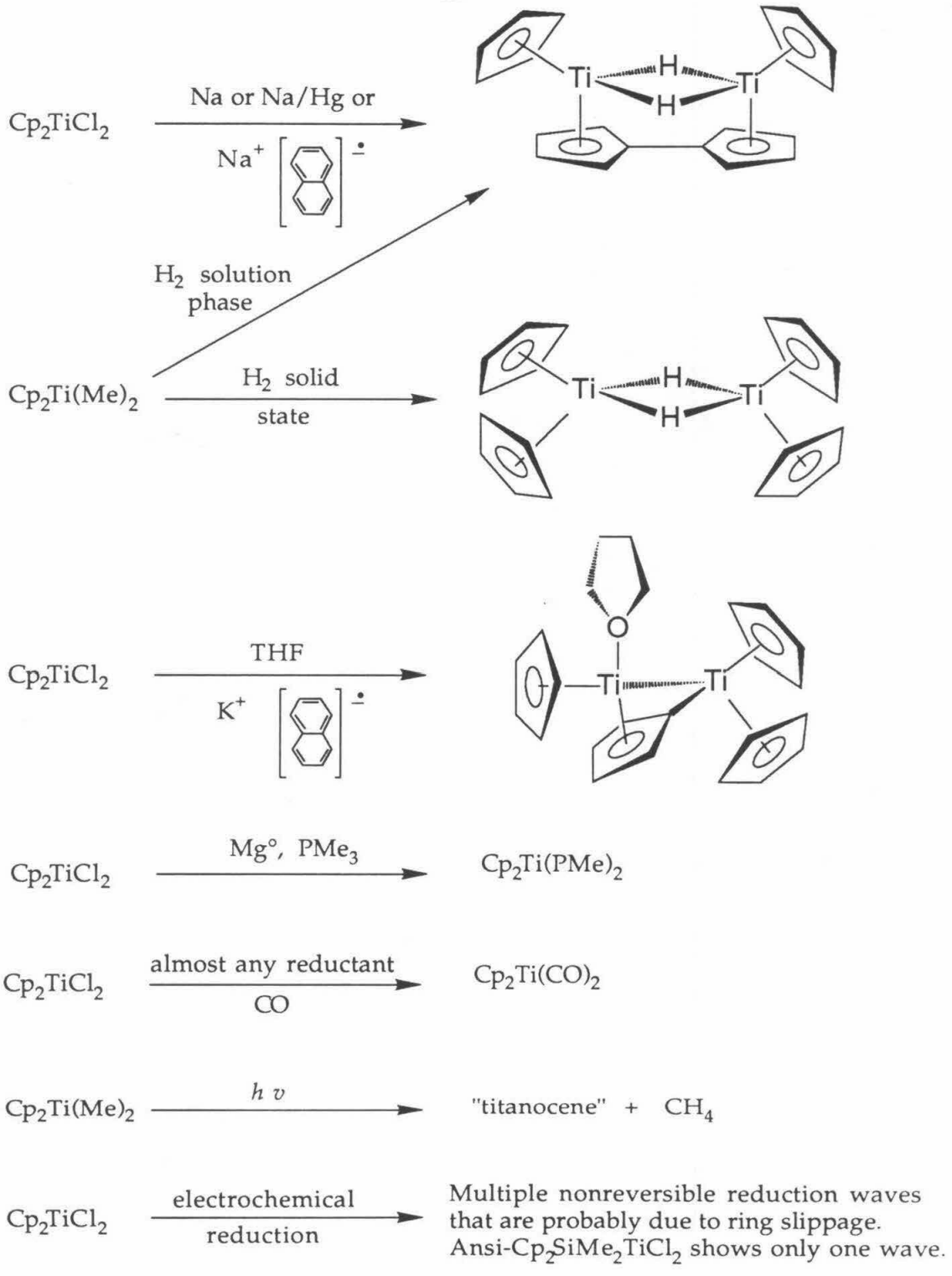


Figure 1. Some of the many routes to "titanocene."

The first discrete compound to be isolated from these many different routes to titanocene was μ-(η^5:η^5-fulvalene)-μ-dihydrido(bis(η^5-cyclopentadienyltitanium)) isolated from the chemical reduction of titanocene dichloride by either sodium, sodium amalgam, or sodium naphthalide. The reaction and postulated mechanism and structure are shown in Figure 2.[3]

This compound does not react with nitrogen, and consequently, is probably not the same "titanocene" responsible for the nitrogen-reduction chemistry that characterizes some of the other routes to titanocene. A route to titanocene that does furnish a material capable of reducing nitrogen is the hydrogenolysis of solid dimethyltitanocene to yield what is believed to be a $[Cp2TiH]_2$ dimer shown in Figure 1. Solution hydrogenolysis gave the fulvalene product isolated by Brintzinger and Bercaw. Almost all routes to titanocene have provided different materials. The only other "titanocene" to be structurally characterized was generated by the reaction of titanocene dichloride with potassium napthalide in THF.[4] The compound is shown in Figure 1. One unifying observation is that all of the routes to titanocene, in the absence of Lewis bases, generate materials in which the cyclopentadienyl ligands are not innocent ligands. That is to say, they participate in the chemistry and do not remain unchanged during the course of the reaction.

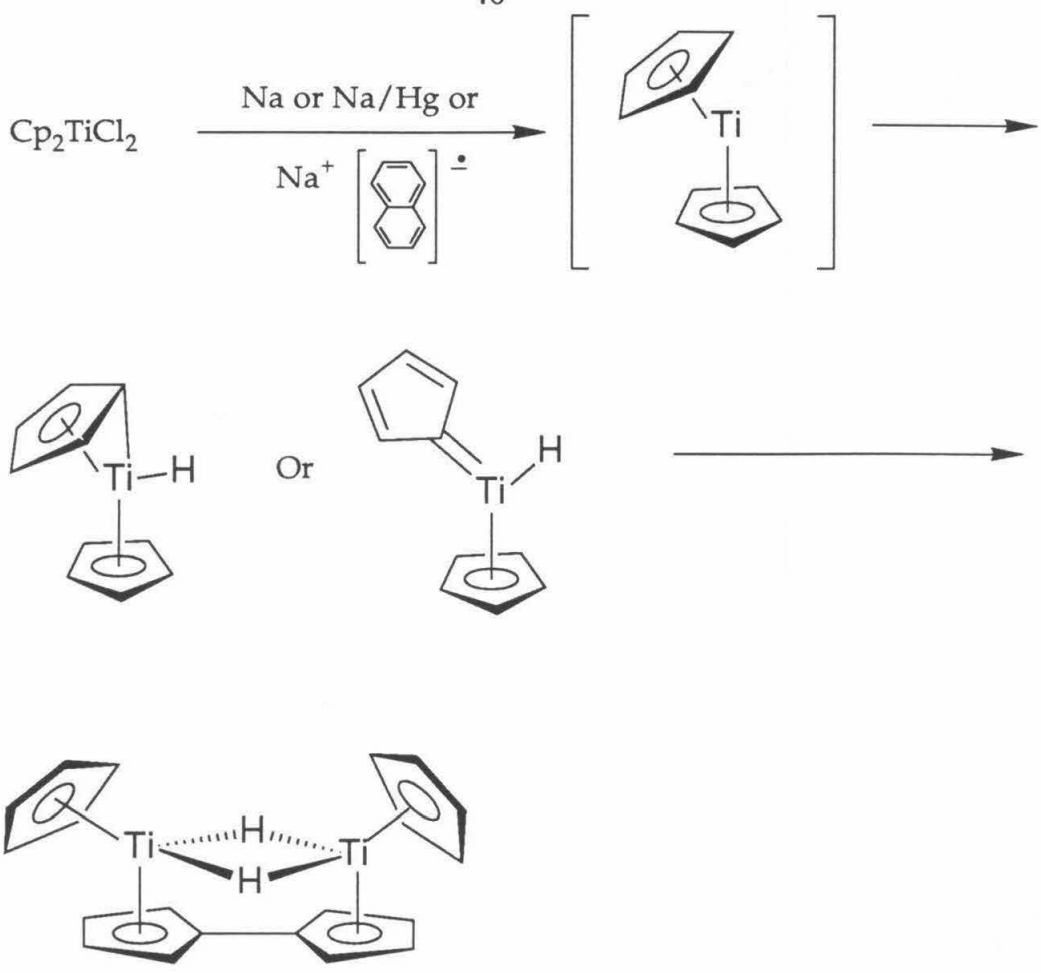


Figure 2. Mechanism of titanium hydride formation in titanocene preparations.

In order to circumvent some of the problems inherent in the titanocene chemistry, alternative sources of titanocene have been sought. Two of the most commonly used "titanocenes" are bis(trimethylphosphine)bis(η^5-cyclopentadienyl)titanium(II) and bis(η^5-cyclopentadienyl)dicarbonyltitanium(II).[5] These compounds are merely Lewis base adducts of the parent titanocene. The materials are typically synthesized by the previously mentioned techniques in the presence of the appropriate Lewis base. Presumably, the Lewis base intercepts the

transitorily stable titanocene before it has a chance to activate cyclopentadienyl rings. The acid/base pair is then stabilized or deactivated with regard to ring activation. One of the attractive features of the these titanocene synthons comes from their tractability. That is to say, the compounds are easily isolated and purified. A problem with the compounds, however, is the presence of the Lewis base during reaction. These ligands tend to deactivate the titanocene. Additionally, only one carbonyl and only one of the phosphines are photochemically labile. This means also that the parent titanocene cannot be generated photochemically at low temperature. Nonetheless, these compounds have been responsible for many interesting materials and reactions. Two examples are the isolation of olefin adducts of monocarbonyltitanocene,[6] and the very recent application of the titanocenebis(trimethylphosphine) to generate vinyl titanium carbenes. Titanocenebis(trimethylphosphine) reacts with 3,3-diphenylcyclopropene to generate a vinylcarbene trimethylphosphine complex of titanocene.[7] These materials may have applications to olefin metathesis.

In the first chapter, the mechanism of the photochemical generation of cyclopropane from bis(η^5-cyclopentadienyl)titanacyclobutanes was examined. Significantly, however, another product of this reaction is a species that behaves as monomeric titanocene. In chapter one, little was said about the organometallic products associated with this photochemical reductive elimination. By mass balance, the organometallic product of the reaction is titanocene, a.k.a. bis(η^5-cyclopentadienyl)titanium. This is borne out by trapping reactions. As was mentioned, a wide variety of traps intercept the titanocene and provide products associated with titanocene. Most notably, photolysis in the presence of trimethylphosphine yields

bis(trimethylphosphine)bis(η^5-cyclopentadienyl)titanium(II) in quantitative yield. Since the titanocene can be generated photochemically, a whole new temperature regime is available to titanocene chemistry. Generating titanocene at low temperature means that the titanocene should undergo the typical ring-insertion reactions more slowly and thereby not only allow more chemistry with a wider range of materials, but also mean higher yields in all reactions, since the competing reactions are slower.

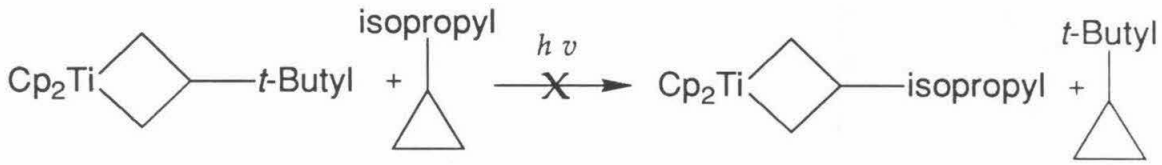
Isoelectronic with titanocene is zirconocene. Zirconocene has received a great deal of attention recently. This is due in part to the discovery that zirconocene is synthetically useful for numerous reductive coupling reactions and transmetallation reactions.[8] Titanocene has not found use in as many synthetically useful transformations despite the fact that it is felt that titanocene is more stable than zirconocene with respect to forming metal hydride bonds.[9] One of the goals of the research was to gain a fundamental understanding of titanocene in order to exploit its synthetic chemistry fully. It is doubtful that photochemical routes to titanocene will be synthetically useful in stoichiometric reactions because of the number of steps needed to synthesize a titanacyclobutane. However, it is felt that the knowledge gained from understanding this very clean, controllable route to titanocene will allow other more economical routes to titanocene to be better and more fully employed. An additional goal of the research was to exploit the reactivity of the uncomplexed (Lewis base-free) titanocene. The extremely clean nature and high yield of the photochemical generation of titanocene from the photolysis of titanacyclobutanes makes it ideal for generating titanocene at low temperatures. Low temperatures are not feasible with the other titanocene sources, since fairly high temperatures are needed to allow the reaction that generates the titanocene to proceed.

These higher temperatures result then in faster decomposition of the titanocene generated.

Results and Discussion:

The chemistry of titanocene has been extensively studied over the past 20 years. Therefore, it was decided to investigate the chemistry of photochemically generated titanocene in order to take advantage of low temperature generation and to take advantage of the fact that the titanocene is generated in the absence of ancillary ligands. While it is believed that the photochemical route to titanocene is extremely clean and efficient, this does not preclude the typical degradation reactions that titanocene is prone to undergo in the absence of traps.

Some of the best and most used Ziegler-Natta olefin polymerization catalysts are based on titanium. Therefore, it was felt that olefin, acetylenes, and dienes would not only be a good series of compounds to explore the chemistry of photochemically generated titanocene, but would also provide a series of compounds to elucidate the fundamental interactions between Lewis acidic metals and unsaturated substrates.



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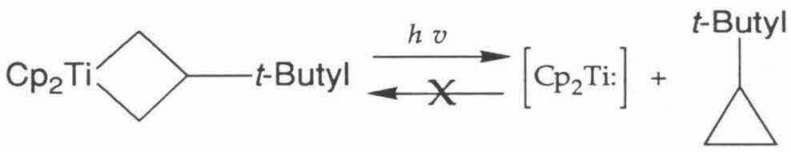


Figure 3. The reductive elimination is irreversible.

Prior to the examination of the interaction of acetylenes with photochemically generated titanocene, a series of control experiments were undertaken to determine the inertness of the cogenerated cyclopropane and the yields with which the titanocene could be trapped. Photolysis of the β-*tert*-butyltitanacyclobutane in the presence of ~20 equivalents isopropylcyclopropane to 50% conversion followed by NMR examination revealed no incorporation of the isopropylcyclopropane in a metallacycle. That is to say, the photochemical extrusion of cyclopropane is irreversible. This reaction is shown in Figure 3.

Photolysis of the neohexene metallacycle in the presence of methyl disulfide (3 eq.) in toluene at -40 °C resulted in formation of the known[10] $Cp_2Ti(SMe)_2$ in quantitative yield. This result indicated that at reasonably high temperatures it was possible to trap the titanocene in high yield without resorting to very high excesses of trap. Figure 4 illustrates this reaction.

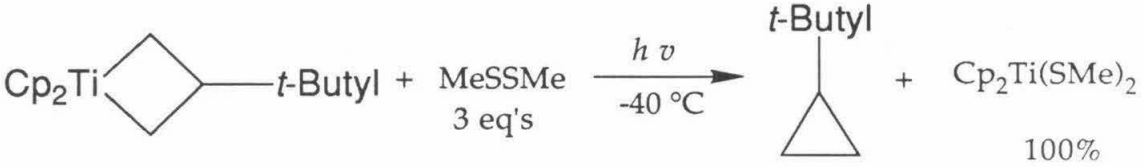


Figure 4. Very high yields are possible using photochemically generated titanocene.

Photolysis at -78 °C of the neohexene metallacycle in the presence of the diphenylacetylene results in quantitative yield of the monoacetylene adduct as determined by NMR. This material, upon warming to temperatures greater than -40 °C, inserts a second diphenylacetylene to

give the known bis(η^5-cyclopentadienyl)tetraphenyltitanacylopentadiene. This reaction is illustraed in Figure 5a.

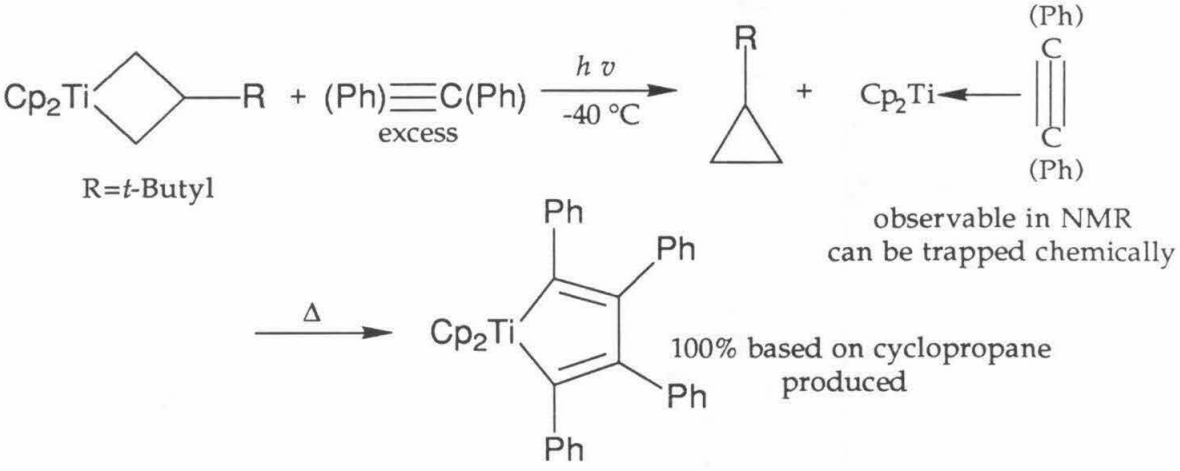


Figure 5a. Reaction of photochemically generated titanocene with diphenylacetylene.

Both the monoacetylene adduct of titanocene and the titanacyclopentadiene seemed to be photochemically inert as evidenced by the repeated failure to observe any secondary photochemical products. However, for either compound a degenerate photochemically induced loss of the acetylene (or less likely, tetraphenylcyclobutadiene), followed by rapid reinsertion, cannot be ruled out. The reaction could be repeated in equally high yield with one equivalent of diphenylacetylene. The reaction proceeded equally well in THF or toluene, Figure 5b.

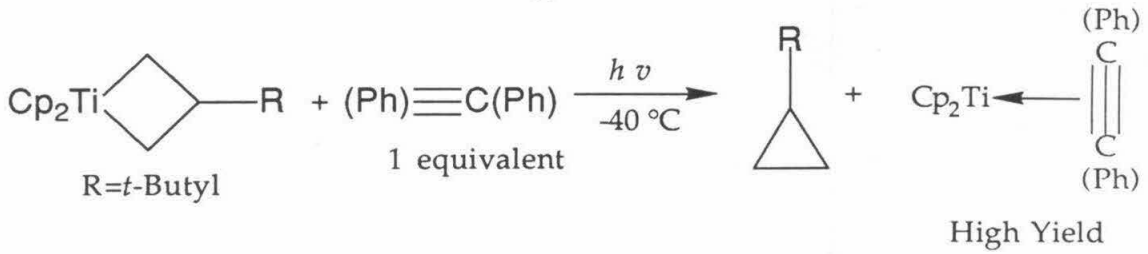


Figure 5b. Titanocene can be efficiently trapped with a stoichiometric amount of diphenylacetylene.

Attempts to repeat the reaction with 2-butyne resulted in formation of the bis(η^5-cyclopentadienyl)tetramethyltitanacyclopentadiene at temperatures as low as -78 °C, Figure 6. Attempts to trap the presumed monoacetylene adduct with such reagents as phosphorus ylides failed. The monoacetylene adduct evidently rapidly inserts a second acetylene even at low temperatures. The chemistry of the monoacetylene adducts of titanocene will be discussed in greater detail later in the chapter.

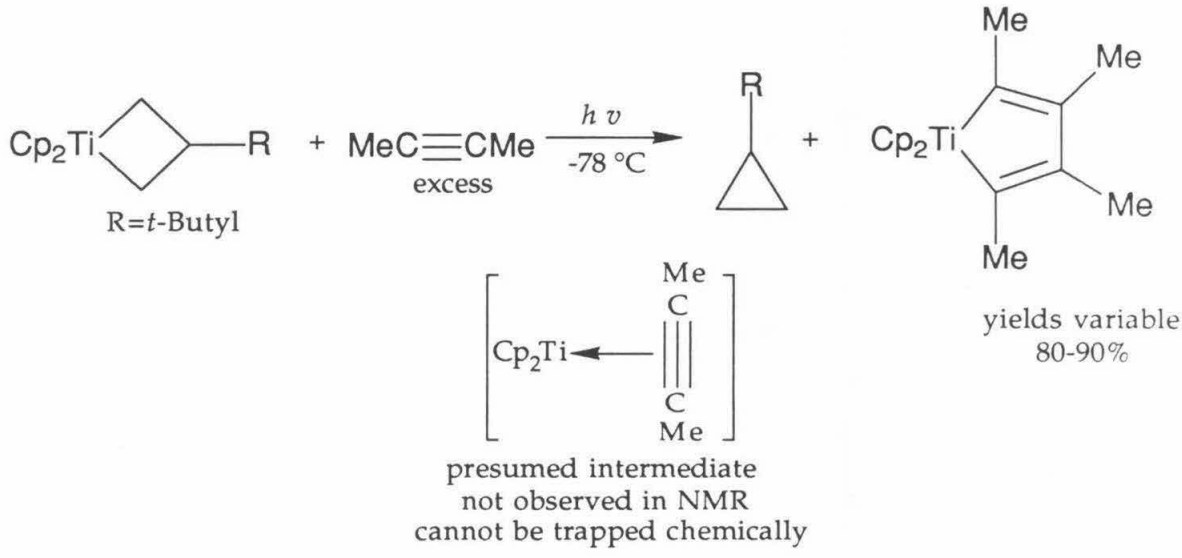
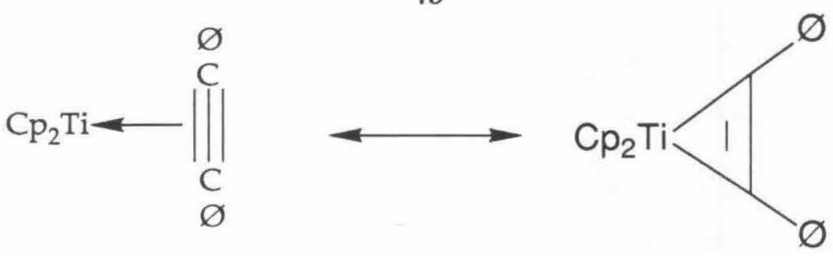


Figure 6. The Reaction of titanocene with 2-butyne.

Acetylenes with large substituents were then investigated so that the rate of addition of the second acetylene would be slower. This change provided additional stability to titanocene acetylene adducts. Acetylenes that were investigated include bis(trimethylsilyl)acetylene, (phenylethynyl)trimethylsilane, di-*tert*-butylacetylene, 1-trimethylsilyl-2-phenyldimethylsilylacetylene. Goals of the investigation were to determine the nature of the interaction between the metal and the acetylene and to develop the chemistry of the adducts. These adducts are particularly interesting, since unlike other acetylene adducts of the early metallocenes, there are no other ancillary ligands such as phosphines and ethers to stabilize the metal complex. This not only maked for more reactive complexes, but was felt to mimic more closely the nature of the interaction between unsaturated substrates and heterogeneous Ziegler-Natta catalysts, which are well known to be passivated by exposure to Lewis bases such as phosphines and ethers.



Lewis acid/base pair

Titanacyclpropene

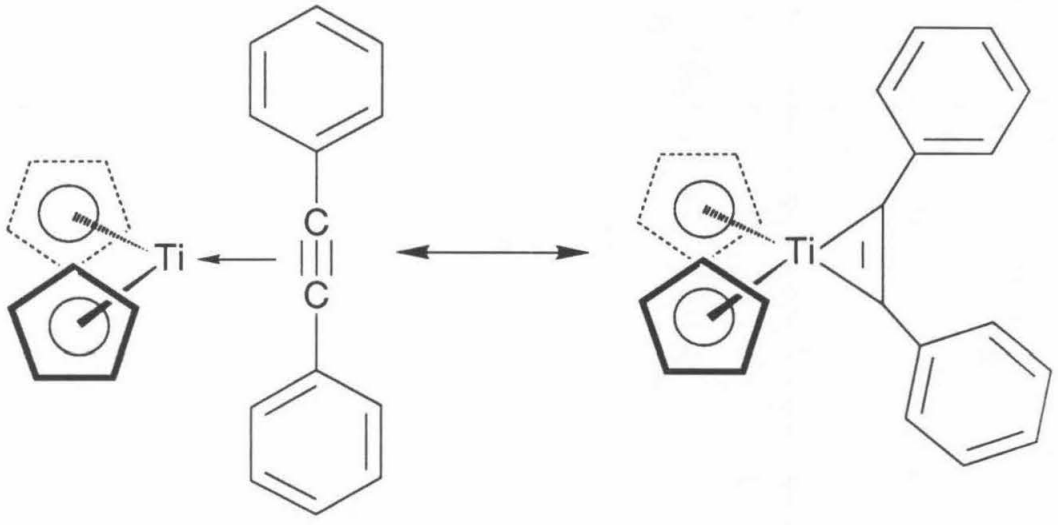


Figure 7. Two modes of bonding in the monoacetylene adducts of titanocene.

One of the first questions addressed was the nature of bonding in the monoacetylene titanocene adduct. The major question to answer was whether the adduct was best described as a Lewis acid/base pair or a titanacyclopropene. These differences are shown in Figure 1. The ideal solution to understanding this question would be through single-crystal x-ray structure determination. Unfortunately, the di-*tert*-butylacetylene adduct of titanocene could not be recrystallized. Excellent crystals of the

$Cp_2Ti(RCCR')$

R	R'	1HNMR(δ)	13CNMR(δ)
Ø	Ø	Cp, 6.17, s, 10H	195.0, q, <u>C</u>Ø
		Ø, 7.5 m	142.3, q, ipso Ø
		Ø, 7.0 m	115.8, d, J_{CH}=172.5Hz, Cp
		Ø, 6.5 m	

<u>Comments</u>: Solvent (deutero toluene) and free diphenyl acetylene obscured the remaining phenyl resonances. In deutero THF the missing phenyl resonances were 143.45, q, ipso of Ø; 128.6; 127.7; 125.84; 115.6 Cp. Yield of the reaction 80%, Temperature in probe -50 °C. 13CNMR of free diphenyl acetylene: 132.27, 129.15, 129.02, 124.28, 90.22 (acetylenic).

TMS	TMS	Cp, 6.34, s, 10H	244.7, q, acetylenic
		TMS, -0.26, s, 18H	117.8, d, Cp
			0.60, s, -Si(<u>C</u>H_3)$_3$

<u>Comments:</u> 1HNMR was recorded in deutero toluene at -65 °C. 13CNMR was recorded in deutero benzene at ambient. The yield of the reaction was >90% at 100% conversion. 13CNMR of free bis(trimethylsilyl)acetylene: 113.86, acetylenic; -0.02, -Si(<u>C</u>H_3)$_3$.

SiØ(Me)$_2$	TMS	Ø, 7.18, m, 5H	246.3, q, acetylenic
		Cp, 6.34, s, 10H	240.2, q, acetylenic
		SiØ(Me)$_2$, s, -0.10, 6H	140.13, q, ipso of phenyl
		$SiMe_3$, s, -0.36, 9H	133.6, phenyl; 117.7, Cp
			0.51, TMS; -0.71, SiØ(<u>Me</u>)$_2$

<u>Comments:</u> 1HNMR and 13CNMR were recorded in deutero benzene at ambient temperature.

^{t}butyl	^{t}butyl	Cp, 6.28, s, 10H	199.8, q, acetylenic
		^{t}butyl, 0.57, s, 18H	115.2, d, J_{CH}=171.3Hz, Cp
			39.85, q, ipso of ^{t}butyl
			31.34, qrt, J_{CH}=125.0Hz, methyl

<u>Comments</u>: Yield 90%. Spectra recorded in deutero toluene at -30 °C. 1HNMR of free di^{t}butylacetylene, 1.20 s. 13CNMR of free di^{t}butylacetylene, 87.1, acetylenic; 31.61, methyl; 27.36, ipso.

Figure 8. NMR data of monoacetylene adducts of titanocene.

bis(trimethylsilyl)acetylene adduct were grown, and the material was found to be thermally stable to 80 °C in solution, but decomposed at 80 °C during a vacuum sublimation. However, these crystals were very thin yellow plates, which were not suitable for x-ray diffraction. Different solvents and different recrystallization conditions did not change the situation. The (phenylethynyl)trimethylsilane adduct was successfully recrystallized, but none of the crystals was found to diffract well. The major question to answer regarding the mode of bonding was whether the adduct was best described as Lewis acid/base pair or a titanacyclopropene. These differences are shown in Figure 7.

Examination of the ^{13}C NMR spectra of the acetylene adducts could not provide information about the degree of hybridization of the acetylene, since the carbons involved were quaternary carbons. However, ^{13}C NMR did reveal some interesting features about the interaction. The NMR data are summarized in Figure 8. Most interesting is the extreme downfield shift of the acetylenic carbon of the bound acetylene. Typically, values representing this large of a degree of deshielding mean that the acetylene was behaving as a four-electron donor to the metal.[11] Because of the stereoelectronic configuration of the metal center this is unlikely. The three metal orbitals all lie in a plane between the cyclopentadienyl ligands, and in order for the acetylene to donate four electrons, not just two, the acetylene would have to bond perpendicularly to this plane. This creates a sterically crowded environment inside the cyclopentadienyl wedge. However, it is possible that the acetylene lies somewhere between in the plane and perpendicular to the plane. To address this question, the asymmetrically substituted acetylene adducts of titanocene were examined. If the acetylene were not lying in the plane, then the cyclopentadienyl rings

of the metallocene would become distereotopic and therefore should have anisochronis chemical shifts. This is not observed for the two asymmetrical acetylenes studied. This observation, however, does not rule out fluxional behavior.

Additionally, the highly deshielded acetylenic resonances suggest that the carbons are very electrophilic. Despite the fact that titanocene is formally d^2, it is still very electrophilic and a strong Lewis acid. In support of this statement, an adduct of titanocene with hexafluoro-2-butyne could not be generated. Presumably, the hexafluoro-2-butyne was too electron-deficient to form a stable adduct of titanocene. The only products of the reaction that were observed were polymer and exploded NMR tubes.

Attempts to characterize the monoacetylene adducts of titanocene by methods besides NMR met with failure. Samples of the monoacetylene adducts of titanocene examined by mass spectroscopy failed to show a parent ion. Only free acetylene was observed. Additionally, elemental analysis never provided satisfactory data confirming the stoichiometry.

The chemistry of these acetylene adducts of titanium was briefly investigated. Acetylene adducts of the early metals have received attention recently because of the large number of synthetic transformations that have been realized.[12] It was decided not to investigate the synthetic applications of the photochemically generated titanocene and titanocene-acetylene adducts, since it is typically used in stoichiometric amounts, and there are synthetically more direct ways to generate titanocene than from the photolysis of metallacycles, although there may be some low-temperature applications that could be uncovered. The bulkier acetylene adducts of titanocene did not insert ketones cleanly. This may be due to the extreme sterics associated with the trimethylsilyl groups. In fact, the

bis(trimethylsilyl)acetylene adduct of titanocene did not even insert ethylene to give the titanacyclopentene. The diphenylacetylene adduct of titanocene, on the other hand, cleanly added acetophenone in 80% yield as expected from similar work by Vol'pin in Ref 12(h). This insertion is shown in Figure 9.

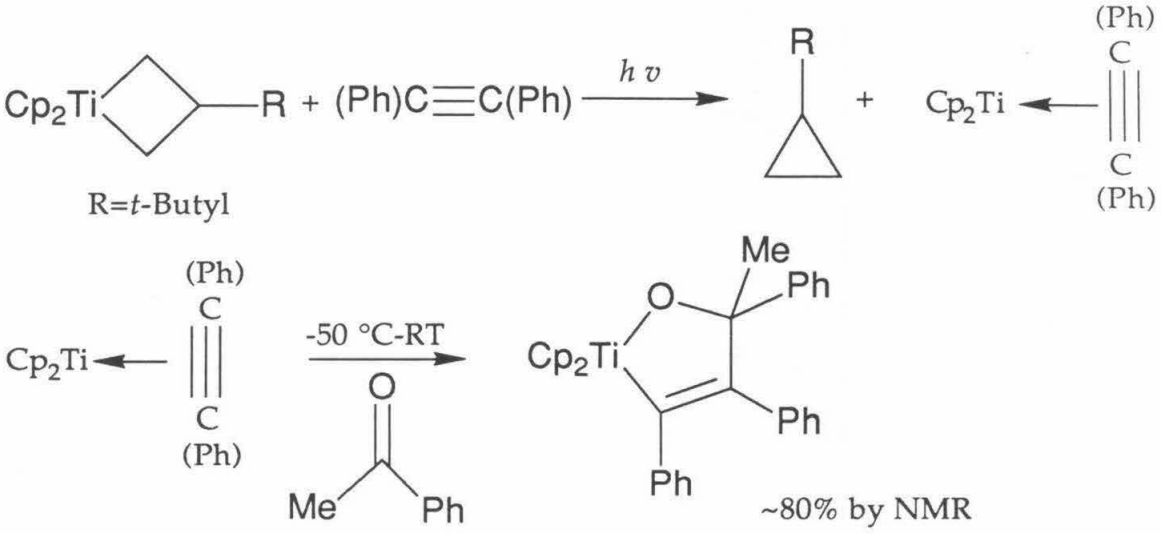


Figure 9. η^2-diphenylacetylenebis(η^5-cyclopentadienyl)titanium inserts acetophenone.

One of the continuing goals of the research was to develop routes to mono- and tri-substituted titanacyclobutenes in order to examine further their photochemistry. One route to this class of compounds would be from methylene transfer to monoacetylene adducts of titanocene. This was realized in the reaction of the bis(trimethylsilyl)acetylene and the diphenyl acetylene adducts of titanocene. Reaction of one equivalent of the bis(trimethylsilyl)acetylene adduct of titanocene with triphenylmethylenephosphorane yielded the titanocene cyclobutene in 100% yield after 15 hours at room temperature, Figure 10. Similarly, reaction of

the diphenylacetylene adduct of titanocene with triphenylmethylenephosphorane initially provided a species that at 0 °C went on slowly to the titanacyclobutene, Figure 10. The intermediate is probably a Lewis acid/base pair, since ylides are very basic and since the acetylene adduct is coordinatively unsaturated. Examples of ylide transfer to metals are relatively rare.[13] While it would be useful to extend the scope of the reaction, this was not realized.

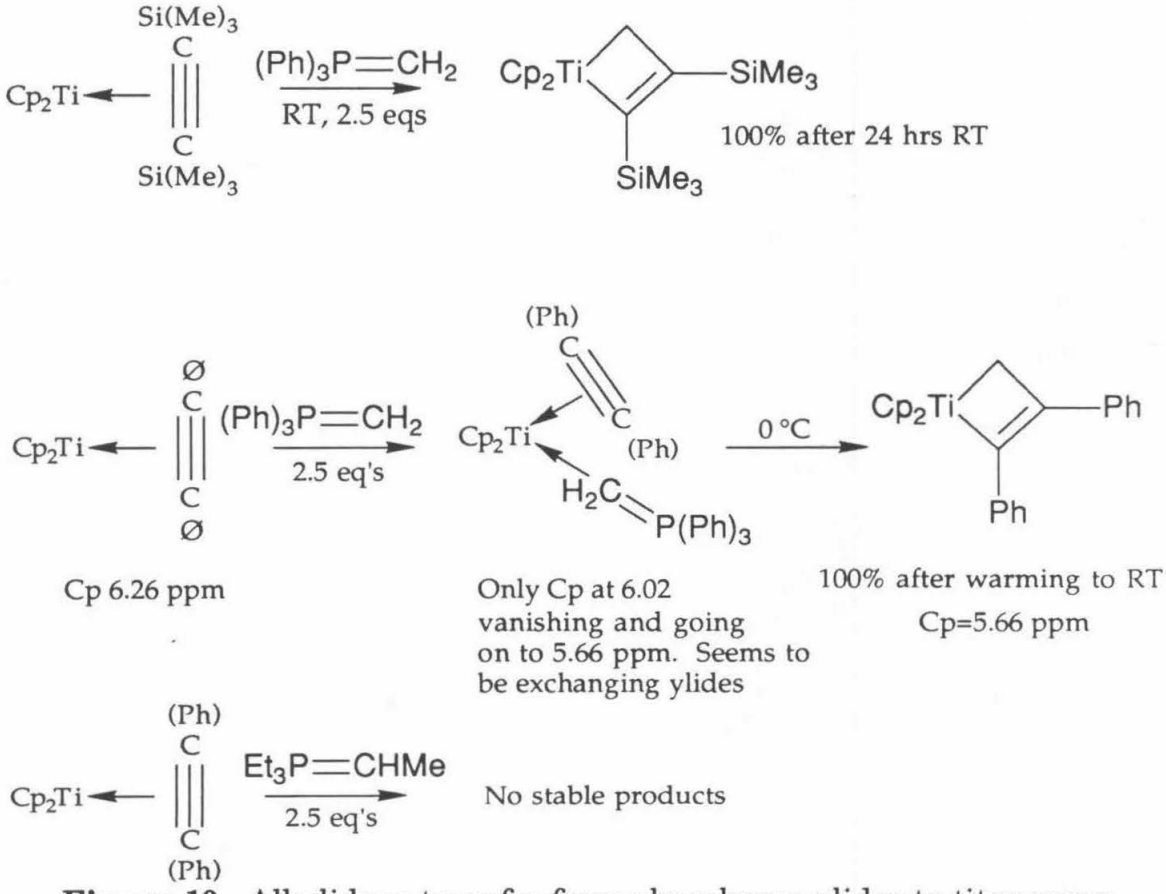


Figure 10. Alkylidene transfer from phosphorus ylides to titanocene monoacetylene adducts.

Reaction of the triethylethylidenephosphorane with the diphenylacetylene adduct failed to yield any tractable products, Figure 10.

This could be due to the the increased basicity of the trialkylphosphoranes. Reaction of trimethylmethylenephosphorane with the di-*tert*-butylacetylene adduct of titanocene also failed to yield any tractable products. Additionally, the desired trisubstituted product will likely be fairly unstable, because of steric interactions from the α position of the metallacycle.

Attempts to transfer the alkylidene moiety of the ylide directly to titanocene also failed with both the trimethylmethylenephosphorane and the triphenylmethylenephosphorane ylide. The reaction was also unsuccessful when the photochemical titanocene was replaced with bis(cyclopentadienyl)titanium(II)bis(trimethylphosphine), photochemically generated from a titanacyclobutane and excess phospine. These two reactions are shown in Figure 11.

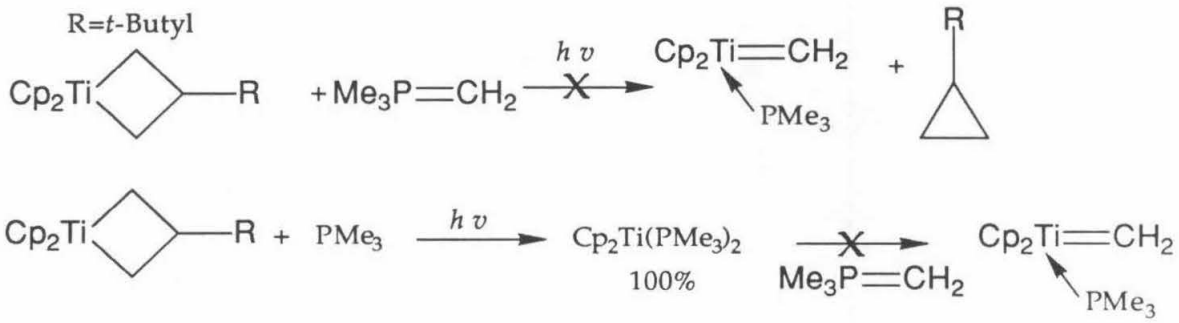


Figure 11. Attempts at alkylidene transfer from phosphorus to titanocene were unsuccessful.

Interestingly, the reaction of titanocene and methylenetriphenylphosphorane yielded only the ethylene adduct of titanocene, Figure 12. This could have resulted from either trapping of photochemically produced ethylene (methylenetriphenylphosphorane

slowly produces ethylene under the photochemical conditions) or from a different mechanism. The ylide could have transferred the methylene, and then the resulting titanium methylidene could have dimerized to the 1,3-dititanacyclobutane, which is known to cleave photochemically to the titanocene ethylene adduct and titanocene.[14] The reaction and two plausible mechanisms are shown in Figure 12. Attempts to intercept the dimethylacetylene adduct of titanocene with an ylide prior to addition of a second acetylene also failed.

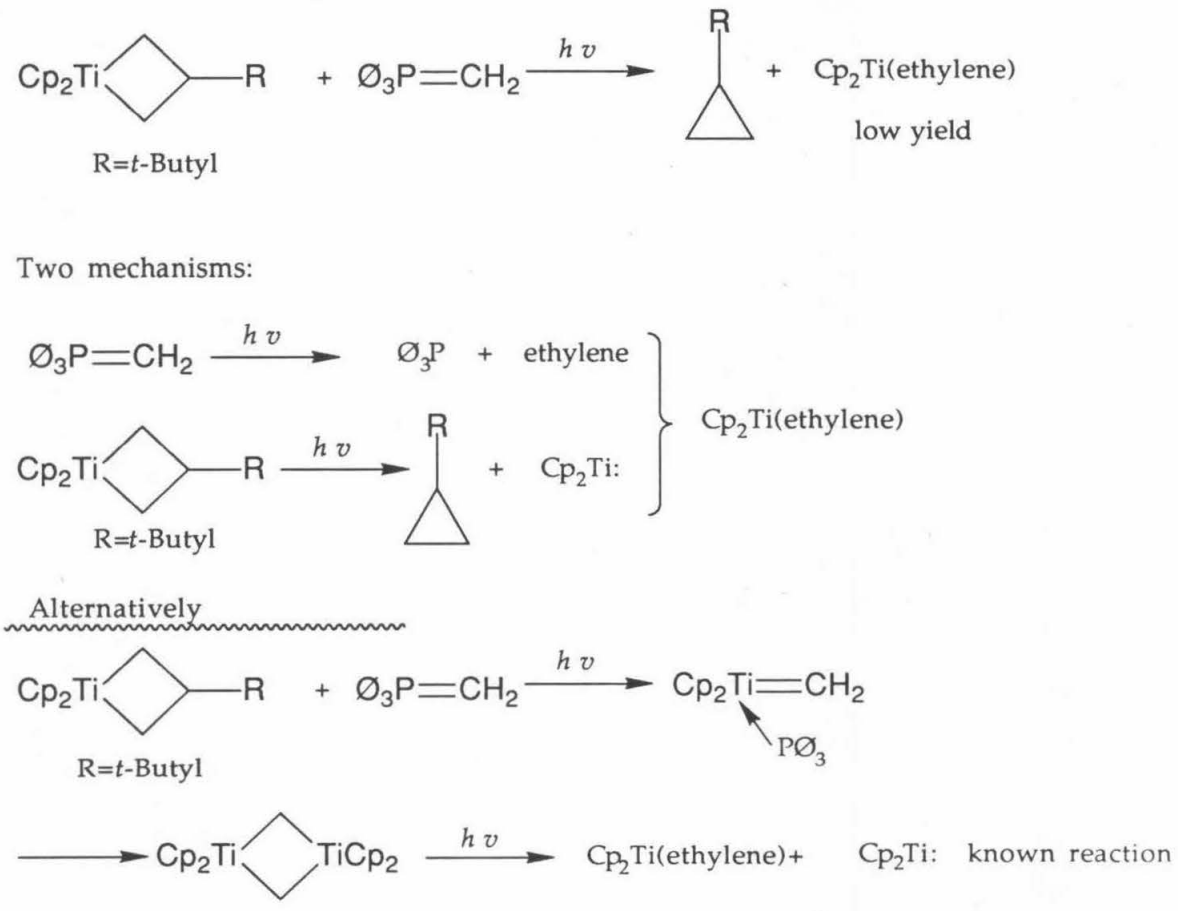


Figure 12. Reaction of phosphorus ylides with titanocene.

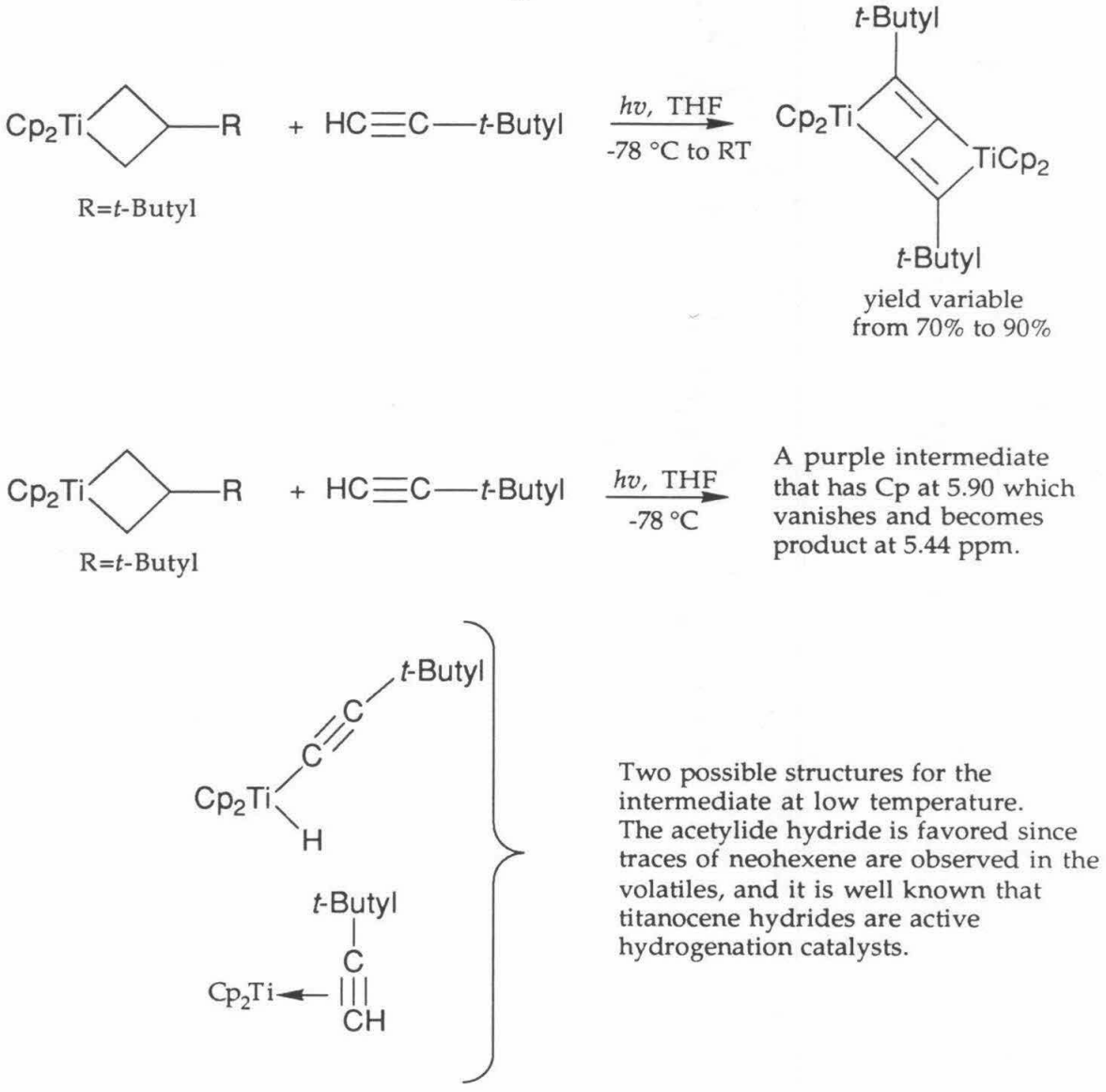
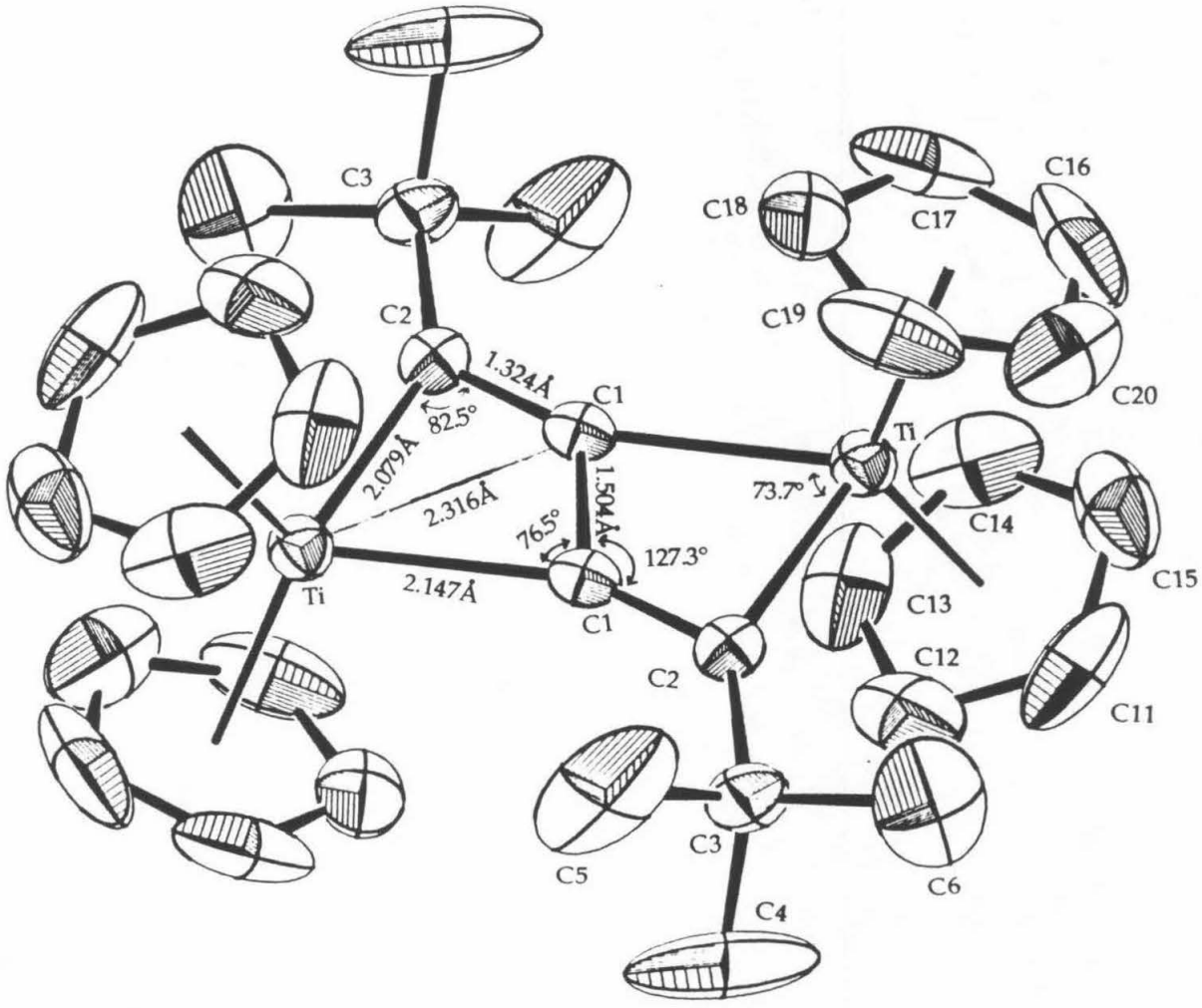


Figure 13. Reaction of titanocene with neohexyne.

Terminal acetylenes were reacted with titanocene at -80 °C. It was hoped that at this temperature a simple acetylene adduct could be formed prior to any thermal chemistry. Only intractable reaction mixtures were obtained from the reaction of phenylacetylene and trimethylsilylacetylene with photochemically generated titanocene. However, at -90 °C a purple

product was formed in ~80% yield from the reaction of excess 3,3-dimethyl-1-butyne with titanocene. This product was not further characterized since even at this temperature it was slowly isomerizing to another green material. The initial material formed is likely to be either an acetylene adduct of titanocene or more likely an acetylide hydride. Traces of 3,3-dimethyl-1-butene were observed in the volatiles of the reaction. The final green product was identified as dimetallabicyclic material shown in Figure 13. The structure of the material was verified by x-ray structure determination. No hydrogens were found on the alpha carbons in the final electron difference map. Additionally, ^{13}C NMR indicated that all of the carbons in the cyclic skeleton were quaternary. Structurally similar materials have been synthesized previously by two methods.[15] The first is by reaction of a 1,3-diacetylene with two equivalents of a titanocene source. The second method is by reaction of the terminal lithium or sodium acetylide with $(Cp_2Ti(III)Cl)_2$. Interestingly, a purple intermediate is also observed in the reaction of the acetylide with Cp_2TiCl. The structure of the product is quite similar to that of the titanacyclobutenes synthesized by Tebbe and coworkers[16] and to the $((MeCp)_2Ti)_2(ø\text{-}CCCC\text{-}ø)$ material synthesized by Stucky and coworkers. The structure is shown in Figure 14. Supplementary x-ray data is included in an appendix in the experimental section. The product is remarkably inert. It fails to insert CO even at elevated pressures and temperatures, unlike the simple titanacyclobutenes.[17] Reaction of phenylacetylene and trimethylsilylacetylene with titanocene yielded product mixtures that were complicated; consequently, the products were not identified. This coupling reaction was not pursued further.

Figure 14. Crystal structure data for μ-(1-3η:2-4η-*trans*, *trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-bis(bis(η^5-cyclopentadienyl)titanium) from the reaction of neohexyne with titanocene.



In addition to acetylenes, the reactivity of olefins with photochemically generated titanocene was investigated. The goal of this chemistry was to develop compounds that could be manipulated to new interesting polymerization catalysts. Specifically, it was hoped that the olefin adducts of titanocene would react with alkylating agents and noncoordinating counter ion acids to give titanium alkyl cations that would likely be very effective olefin-polymerization catalysts.[18] Additionally, it was hoped that trisubstituted metallacycles could be synthesized from the reaction of substituted ylides with internal olefins. Trisubstituted metallacycles would cleave in a 2+2 manner to give a substituted titanium alkylidene. These are very desirable olefin metathesis catalysts. These possible reactivity pathways are shown in Figure 15.

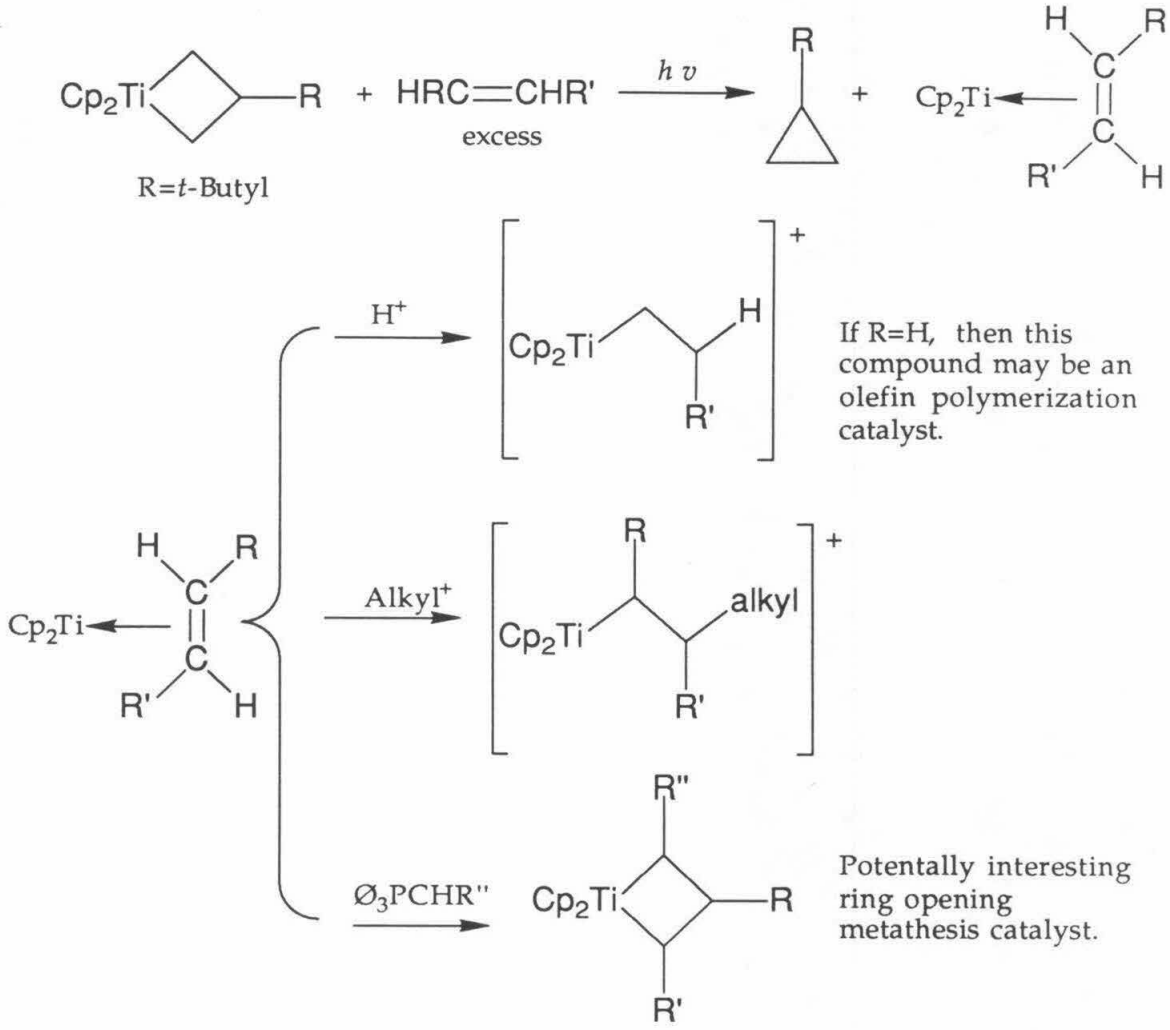
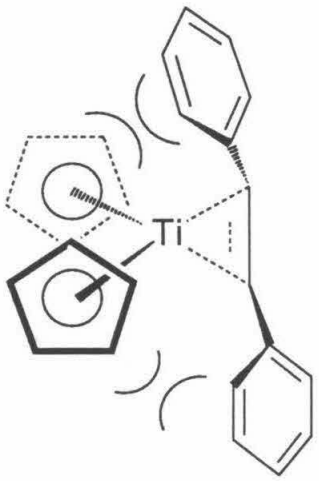


Figure 15. Possible applications of olefin adducts of titanocene.

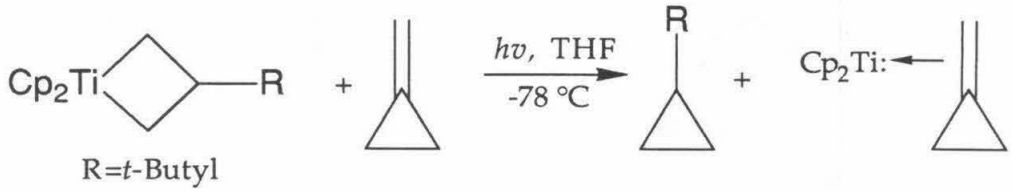
Unlike the acetylenes, increasing the steric bulk of the olefins destablized the olefin titanocene adducts. This was not altogether an unexpected result, given the different electronic configuration of olefins and acetylenes. Substituents on the side-bound olefin would point directly into the cyclopentadienyl rings, Figure 16. The only disubstituted olefin adduct to be stable enough for NMR analysis was derived from stilbene. Olefin



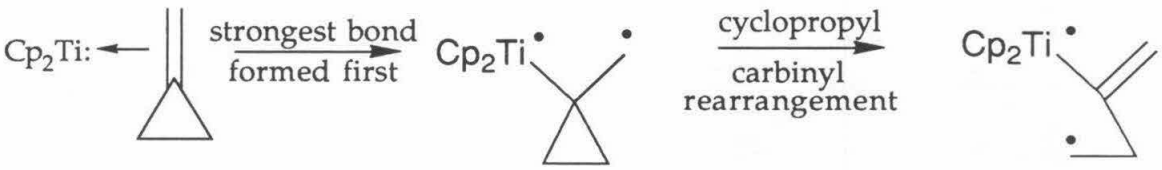
Nature of steric effects that destabilized olefin adducts of titanocene. No chemistry of the olefin adducts could be explored because of their instability.

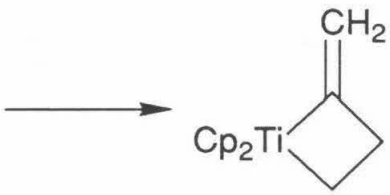
Figure 16. Origin of stereoelectronic effects that destabilized monoolefin adducts of titanocene.

adducts could not be synthesized from titanocene and 3,3-dimethyl-1-butene, allene, and isobutylene. Adducts were successfully synthesized from trans-stilbene, ethylene, propene, and 3-methyl-1-butene. None of these adducts were stable at room temperature. Therefore, none of them could be isolated and characterized by any methods besides NMR. Zirconocene adducts of stilbene have been employed in synthetic chemistry.[19] The ethylene adduct seems to be exchanging ethylenes at low temperature. However, on warming, the yield of titanacyclopentane is 85%.



Possible mode of reaction





exo-methylene titanacyclo-butanes are known species

Neither the olefin adduct of titanocene nor the rearranged product is observed upon reaction of methylenecylcopropane and titanocene.

Figure 17. Possible probes of titanocene olefin interaction.

The attempt to synthesize the methylenecyclopropane adduct of titanocene was undertaken to learn more about the electronic structure of titanocene. A possible rearrangement is shown in Figure 17. Neither this rearrangement nor the simple olefin adduct was observed. This olefin adduct may be unstable under the conditions used in this experiment.

Cp_2Ti(olefin)

Olefin	1H NMR(δ)	13C NMR(δ)
trans-Stilbene	6.06, s, 10H, Cp	107, d, J_{CH}=143.8 Hz, CHØ
	4.52, br s 2H, CHØ	119.2, d, J_{CH}=173.7 Hz, Cp
		151.6, q; 160.3; 123.0; 126.8 Ø's

Comments: Deutero toluene, -30 °C. Yield 100%. Free trans-stilbene in chloroform, 136.9, q; 128.4, d, 160 Hz; 127.3, d, 161.4 Hz; 126.22, d, 158 Hz.

Propene	6.29, s, 5H, Cp,	117.3, d, J_{CH}=177.5 Hz, Cp.
	6.27, s, 5H, Cp	116.8, d, J_{CH}=177.5 Hz, Cp.
	3.88, br mult, 1H	116.3, d, J_{CH}=144.5 Hz, CH.
	2.40, d, 1H, J=8.8Hz	101.6, t, J_{CH}=145.6 Hz, CH_2.
	1.80, d, 1H, J=10.74	25.88, qr, J_{CH}=120.3 Hz, CH_3.
	0.80, s, 3H,	

Comments: Deutero toluene at -78 °C. Methyl of propene overlapped the *tert*-butyl group of the cyclopropane. Free propene 13CNMR: 115.6, CH2; 133.6, CH2; 19.7, methyl.

3-Methyl-	6.69, s, 5H, Cp.	3.75, 1H
1-Butene	6.66, s, 5H, Cp.	2.87. 1H
	6.00, 1H	1.83, 1H
		0.47, 3H

Comments: The adduct was tentatively assigned. It was unstable even in THF at -80 °C. Free ligand, 1HNMR: 5.77, m; 4.94, d, J=17.4 Hz; 4.84, d, J=10.0 Hz; 2.25, b, isopropyl; 0.97, d, 6H, J=6.1 Hz.

Ethylene	6.24, s, 10H, Cp	13CNMR: can't
(toluene)	5.29, s, broad, free ethylene	be unambiguously
	1.62, s, bound ethylene	assigned.

Comments:Ethylenes seemed to be exchanging at -78 °C in both THF and Toluene. Yield low, but on warming, 83% titanacyclopentane observed.

Figure 18. NMR data for olefin adducts of titanocene.

No other materials (cyclobutane) were observed after extended photolysis. The NMR data for the olefin adducts are presented in Figure 18. The most interesting feature of the table is the coupling constants for the olefin adducts. The hybridization is intermediate between that of an sp^2 and an sp^3 carbon. This indicates that the structure is intermediate between the two limiting structural isomers, the olefin adduct of a metal, and a metallacyclpropane. This is similar to what has been observed in other systems.[20] The instability of the olefin adducts of titanocene precluded a detailed examination of their chemistry. Attempts to alkylate olefin adducts at -78 °C with $Me_3O^+BF_4^-$ resulted only in paramagnetic products. Despite the lack of subsequent chemistry, the observed olefin adducts represent a new class of compounds previously unknown.

The reaction of photochemically generated titanocene with butadiene generated an adduct that was much more stable than than the monoolefin adducts. The product could be taken to dryness under vacuum at room temperature without decomposition. The NMR data are tabulated in Figure 19. Typical NMR spectra associated with the synthesis of the 1,3-butadiene adduct of titanocene are shown in Figures 20 and 21. They serve to demonstrate how clean and efficient the reaction is. The coupling constants indicate that the material is a butadiene adduct of titanocene and not a titanacyclopentene. Additionally, there appears to be no fluxional behavior. No changes in NMR spectra were observed on warming from -78 °C to ambient. This is in contrast to the zirconocene diene adducts, which exhibit isomerization between the s-cis and s-trans forms.[21] The butadiene adduct of titanocene can not be in the s-cis form, since this would place the two cyclopentadienyl ligands in different environments, and only

Cp_2Ti(diene)

Diene	1HNMR(δ)	13CNMR(δ)
1,3-butadiene	4.95, s, 10H, Cp	99.5 d, J_{CH}=172.4 Hz, Cp.
	3.32-3.19, m, 4H	97.8, d, J_{CH}=157±2.5 Hz, $\underline{C}H$.
	1.31, m, 2H	68,9, t, J_{CH}=155.2 Hz, $\underline{C}H_2$.

Comments: Deuterated THF at 0 °C, yield 98%. Free butadiene: 13CNMR, 138.7, J_{CH}=162.9 Hz, $\underline{C}H$; 118.0, J_{CH}=157.4 Hz, $\underline{C}H_2$. The THF in the 13CNMR spectra was broad indicating exchange. The bound butadiene protons exhibited second-order coupling constants.

1,3-butadiene	4.63, s, 10H, Cp	99.04, d, J_{CH}=172.4 Hz, Cp
	3.17, br s, 4H	97.6, d, J_{CH}=157.0 Hz, $\underline{C}H$
	1.28, d, 2H, J=11.2 Hz	69.3, t, J_{CH}=155.9 Hz,$\underline{C}H_2$

Comments: Spectra were acquired in deutero benzene at ambient. From isolated material from preparation in THF. No THF present in NMR. Slow decomposition at room temperature.

1,3-pentadiene	4.96, s, 5H, Cp
	4.97, s, 5H, Cp
	3,30, t, 1H, J=13 Hz
	2.97, d, 1H, J=7.3 Hz
	2.80, m, 1H
	1.94, m, 4H, (overlapping methyl and mult.)
	1.10, d, 1H, J=15.8 Hz

Comments: NMR was taken at -78 °C in THF. The material was not stable above -40 °C. No carbon data were acquired because of the instability of the material.

Figure 19. NMR data for diene adducts of titanocene.

a single cyclopentadiene resonance is observed in the NMR spectrum. The remainder of the spectrum was second order and could not be completely assigned. Reaction of trans-1,3-pentadiene with titanocene generated a product with less thermal stability than that formed from butadiene. The product was characterized only by proton NMR, and the data are shown in Figure 19. Attempts were undertaken to generate adducts of titanocene with isoprene and 1,3-cyclohexadiene, and trans,trans-1,4-diphenyl-1,3-butadiene, and 1,4-pentadiene. None of these materials gave titanocene diene adducts. The volatile organic products from the cyclohexadiene reaction included benzene and cyclohexene. The volatiles from the reaction of 1,4-pentadiene with titanocene were predominantly 1,3-pentadienes. The fact that hydrogen transfer occurred is not surprising, given that titanocene is a very active hydrogenation catalyst. The lack of reactivity of titanocene with isoprene and trans,trans-1,4-diphenyl-1,3-butadiene was surprising in that the isoelectronic zirconocene complexes are known. The result was rationalized in terms of the smaller size of titanium. The sterics associated with the bent metallocenes are too great to allow adduct formation in the case of titanocene. No x-ray quality crystals of the butadiene titanocene complex could be grown.

The simple oxidative insertion chemistry of titanocene was investigated. As mentioned, titanocene inserts into disulfides to give, in excellent yield, the titanocene dithiolates. Titanocene did not react with trimethylsilane, chlorotrimethylsilane, and trimethylsilyl azide. Titanocene reacted with carbon disulfide, and acetonitrile to give paramagnetic products, which were not characterized.

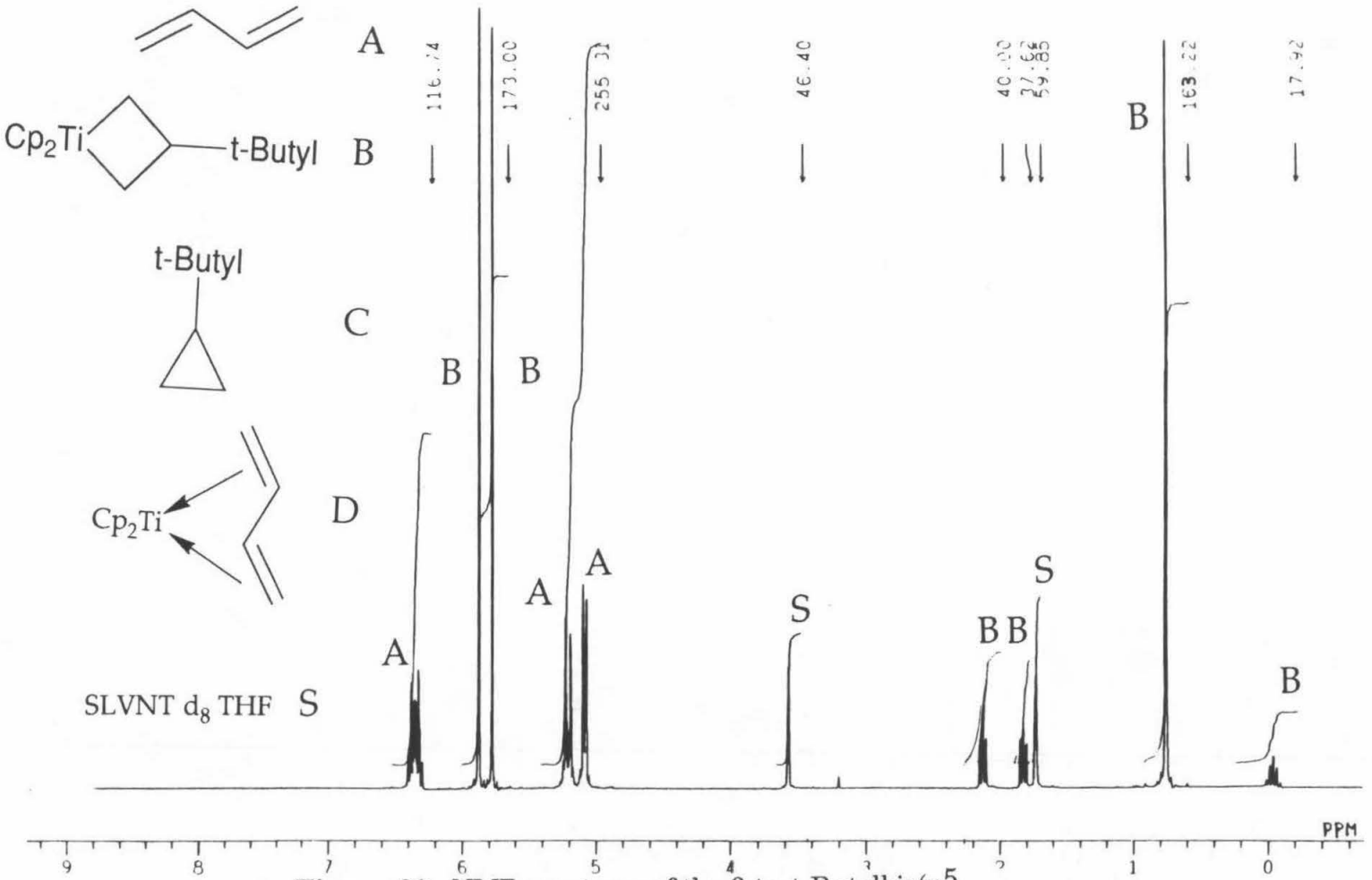


Figure 20. NMR spectrum of the β-tert-Butylbis(η^5-cyclopentadienyl)titanacyclobutane and 1,3-butadiene prior to photolysis.

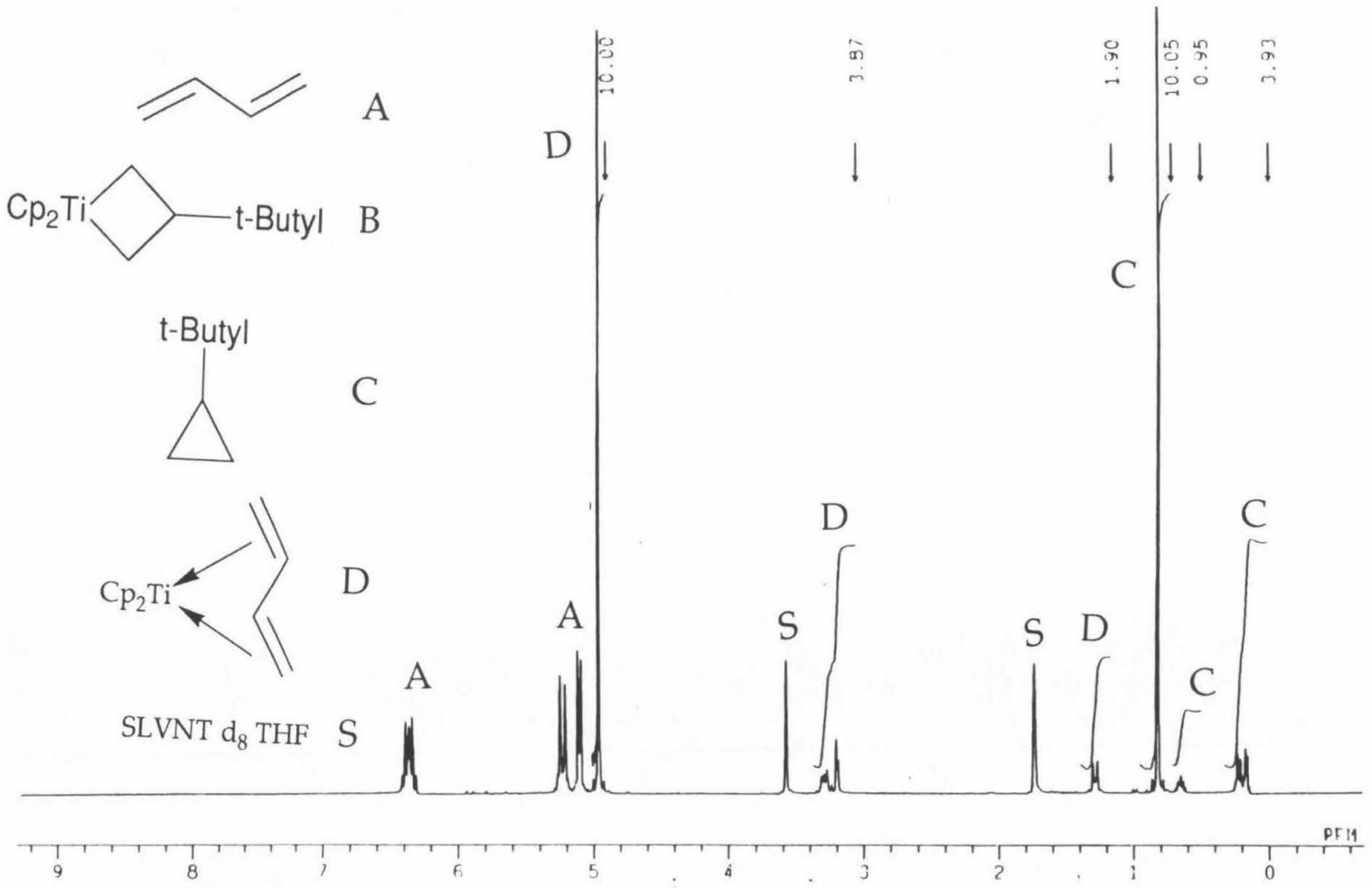


Figure 21. NMR spectrum of titanocene(η^4-butadiene). This is the same NMR sample as Figure 20 after photolysis.

In conclusion, a series of olefin and acetylene adducts have been synthesized without the benefit of ancillary ligands on the metal. It was found that increasing the steric bulk of the acetylenes led to complexes that were increasingly stable. However, the olefin adducts were invariably unstable. The chemistry of the acetylene adducts is very much what one would expect for a sterically demanding environment around the metal. Some of the acetylene adducts were found to insert unsubstituted ylides. The olefin adducts were too unstable to exploit their chemistry. However, the low temperature photochemical route to titanocene led to a series of olefin and diene adducts of titanocene. It is unlikely that these compounds could have been accessible via other titanocene chemistry.

Experimental Section:

General Procedures. All work involving air- and/or moisture-sensitive compounds was performed using standard high-vacuum or Schlenk-line techniques under argon purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Work involving manipulation inside of a drybox was performed under nitrogen in a Vacuum Atmospheres drybox equipped with a -40 °C refrigerator and a dry-cool recirculator. Proton and carbon NMR spectra were recorded on a JEOL FX-90Q (89.9 MHz ^{1}H, 84.72 MHz ^{19}F, 36.98 MHz ^{31}P, 22.5 MHz, ^{13}C), and a JEOL GX-400 (399.65 MHz ^{1}H, 61.35 MHz ^{2}H, 100.67 MHz ^{13}C), and on a Varian EM-390 (90 MHz ^{1}H) and on a Varian XL-200 (200 MHz, ^{1}H). Proton chemical shifts are referenced to internal residual protiosolvents. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Deuterium chemical shifts are referenced to natural abundance deuterium in the solvent. Phosphorus was referenced to an external phosphoric acid standard. UV-vis spectroscopy was performed with a Hewlett-Packard 8154A diode array spectrophotometer. Gas chromatography analyses (VPC) were performed on a Shimadzu GC-Mini 2 flame ionization instrument with a 50 meter capillary column and equipped with a Hewlett-Packard model 339A integrator. Preparative VPC was performed on a Varian 920 Aerograph with a thermal conductivity detector equipped with a Hewlett Packard 7127A strip recorder (columns: 6 ft by 1/4, SE-30 or a 4 ft by 1/2 , silver nitrate). Thin layer chromatography (TLC) was performed on precoated TLC plates (silica gel 60 F-254, EM Reagants). Elemental analysis was performed at the analytical facilities of the California Institute of Technology or at Gailbraith Labs. Photolyses

were performed with a 450 watt high-pressure, mercury Hanovia Lamp. Temperatures were maintained with clear pyrex dewars filled with isopropanol at the desired temperature. Temperatures cited reflect the final temperature that the bath obtained at the end of photolysis; typically, a change of only 10 degrees was observed. All photolyses were obtained in pyrex glass unless otherwise stated.

Materials. The solvents were purified as follows: toluene, benzene, tetrahydrofuran, and diethyl ether were distilled under vacuum from sodium benzophenone ketyl into solvent flasks equipped with Teflon screw-type valves, methylene chloride, acetonitrile, chloroform, pyridine were distilled from calcium hydride at atmospheric pressure and subsequently freeze-pump-thaw degassed. Dimethylsulfoxide was distilled from calcium hydride at reduced pressure. Diphenylacetylene, stilbene, and 1,4-diphenyl-1,3-butadiene were recrystallized prior to use. All volatile acetylenes were distilled and degassed prior to use. Solvents used in photochemical reactions (typically, THF, benzene, toluene, and 2-methyltetrahydrofuran) were vacuum-distilled directly into the reaction vessels from sodium-potassium alloy and were thoroughly degassed prior to use. Bis(cyclopentadienyl)-ß-*tert*-butyltitanacyclobutane (neohexene titanacyclobutane) was synthesized from adaptations of literature procedures[22], and carefully recrystallized from diethyl ether prior to use and stored at -30 °C in a freezer in a drybox. The following gases were used as received after freeze-pump-thaw degassing on a high-vacuum line: ethylene, propene, trimethylsilane, allene, isobutylene, butadiene, 1,1,1,3,3,3-hexafluoro-2-butyne, 3-methyl-1-butene. The following compounds were distilled with careful attention to appropriate drying prior to use: iodomethane, methyl disulfide, isopropylcyclopropane, acetonitrile,

methylene chloride, trimethylsilyl azide, chlorotrimethylsilane, 3,3-dimethyl-1-butene, acetophenone, styrene, methylene cyclopropane, trimethylphosphine, isoprene (2-methyl-1,3-butadiene), 1,4-pentadiene, 1,3-cyclohexadiene, bis(trimethylsilyl)acetylene. di-*tert*-butylacetylene was synthesized from the literature procedure[23] and was purified by preparative gas chromatography. 1-Trimethylsilyl-2-(dimethylphenylsilyl)acetylene was prepared from lithium trimethylsilylacetylide and chlorodimethylphenylsilane, and was purified by distillation.

General preparative Scale Photolysis: η^2-bis(trimethylsilyl)acetylene bis(η^5-cyclopentadienyl)titanium: A large glass ampoule equipped with an integral teflon Kontes valve and stir bar was flame-dried under vacuum. In a drybox, 125.0 mgs of the neohexene titanacyclobutane were added. On a vacuum line, ~15 mLs of toluene were vacuum-transferred from NaK. The bis(trimethylsilyl)acetylene, 500.0 mgs (2.94 mmole, 6.5 eq) was vacuum transferred. The entire reaction mixture was freeze-pump-thaw (0 °C) degassed three times. The mixture was photolyzed with stirring at -40 °C for 3 hours, after which time the solution was yellow. The solvent and excess acetylene were removed under vacuum. Pentane (5 mLs) was vacuum-transferred into the flask. In a drybox, this solution was filtered through a glass pipet filled with glass wool into a Schlenk flask. Slow cooling to -78 °C yielded clear, thin, yellow plates. Attempts to cannulate solutions of the acetylene adducts of titanium resulted in decomposition of the titanocene adduct. This same procedure was used to prepare preparative amounts of the η^2-di-*tert*-butylacetylenebis(η^5-cyclopentadienyl)titanium, which could not be recrystallized, and to prepare the η^2-trimethylsilyl(phenyldimethylsilyl)acetylene bis(η^5-cyclopentadienyl)titanium.

General NMR Synthesis of olefin adducts of Titanocene: The following procedure is typical for all NMR experiments aimed at producing olefin adducts of titanocene. A flame sealable NMR tube was charged in a drybox with 7.0 mg of the neohexene titanacyclobutane (25 μmole). On a vacuum line, 450 μL of d_8 toluene were vacuum-transferred from NaK into the NMR tube. A gas-measuring bulb was filled with freeze pump thaw degassed propene. The propene (96.4 μmole) was then condensed into the NMR tube. The NMR spectrum of the reaction mixture was recorded at -60 °C in the NMR probe prior to photolysis. Photolysis was carried at -78 °C. NMR spectra were taken periodically throughout the photolysis. Typically, depending on the optical density of the product, 1 hour of photolysis per 10 mgs of titanacyclobutane were required. The conversion was measured by integrating the remaining starting material vs the *tert*-butylcyclopropane formed. The yield of the reaction was calculated by integrating the *tert*-butylcyclopropane formed vs the product. Mass loss was calculated by integrating the residual solvent signal and using it as an internal standard. Mass loss was typically negligible. Spectral data and yields for the olefin adducts successfully synthesized are presented in the text.

η^2-(Diphenylacetylene)titanocene: A septum-capped NMR tube was charged in a drybox with 10.0mg of the neohexene titanacyclobutane (36 μmole), and 12 mg of diphenylacetylene (67 μmole) and 450 μL of d_8 toluene. The NMR tube was then quickly removed from the drybox and placed in a -78 °C dewar. The photolysis, approximately 1 hour, was carried out at -50 °C or colder. Above this temperature a second diphenylacetylene inserted into the red η^2-diphenylacetylenetitanocene to give the green photochemically inert titanacyclopentadiene. Additional reagents were then added through the septum by syringe. The reaction was successful

even with a 1:1 equivalence of the titanacyclobutane and the diphenylacetylene. Extended photolysis does not seem to be a consideration in the generation of the acetylene adduct as no additional products are observed even when the photolysis is continued briefly past the point of total consumption of starting material.

μ-(1-3η:2-4η-*trans,trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-bis(bis(η^5-cyclopentadienyl)titanium From the Reaction of Neohexyne and Titanocene, Preparative Scale: A glass ampoule with an integral Kontes valve was charged with 155 mgs of the neohexene metallacycle (561 μmole). On a vacuum line, 20 mLs of THF was vacuum-transferred onto the metallacycle. Into the reaction mixture was next transferred, 263.7 mgs of 3,3-dimethyl-1-butyne (3.20 mmole, 5.7 eq). The reaction mixture was warmed to -78 °C and irradiated at -78 °C for 8 hours with stirring. Upon warming to room temperature the dark purple brown solution became turquoise. The reaction mixture was pumped to dryness, and the resulting solid was washed twice with 5 mLs of pentane. The solid was then recrystallized from diethyl ether and THF to provide analytically pure crystals, which were used for single-crystal, x-ray structure determination. ^{1}H NMR, C_7D_8: δ 5.32, s, 10H; 1.22 s 9H. ^{13}CNMR, d^8 dioxane: δ 234.2 q; 125.1 q; 106.7, d, J_{CH}=170.8Hz, Cp; 42.65, d, J_{CH}=125.7Hz, *tert*-butyl methyls; 32.7, q, *tert*-butyl ipso. X-ray crystallography data are shown in the appendix.

Methylenetrimethylphosphorane: A 1000 mL round-bottomed flask fitted with a septum and a stir bar was charged with 200 mLs of diethyl ether. After cooling to -78 °C, a solution of 20 g of methyl bromide in 50 mLs of 0 °C ether was added by cannula. To this solution was then cannulated ~4.0 mL (0.05 mmole) of PMe_3 in 10 mLs of ether. A white precipitate was

formed. The reaction mixture was stirred 12 hours, after which time it was filtered. The tetramethylphosphonium bromide was washed with 20 mLs of ether and then dried under vacuum to yield 5.4 g (31.6 mmole) of product. In a drybox a Schlenk flask was charged with the phosphonium salt and 0.80 g of sodium hydride (33.0 mmole). Outside the box, 70 mLs of THF was added by cannula. The reaction mixture was refluxed for 12 hours. The solids were removed by centrifuging. The THF was removed by distillation. The product was distilled at 120 °C (1.0 g, 11.0 mmole, 34%). ^{1}HNMR, C_6D_6: δ 0.92 d J_{PH}=12.5, 9H; 0.04 d J_{PH}=7.08, 2H.

Ethylidenetriethylphosphorane: A Schlenk flask was charged with 100 mLs of THF and 25 mLs of ethyl bromide (0.33 moles, 8 eq). To this was cannulated approximately 5 mLs of triethylphospine (42 mmole). After 24 hours the white precipitate was isolated, washed and dried under vacuum. In the drybox, a Schlenk was charged with 11.7 g of tetraethylphosphonium bromide (51.5 mmole) and 2.0 g of sodium hydride (83.3 mmole, 1.6 eq). To this was cannulated 100 mLs of THF. The reaction mixture was refluxed for 48 hours. The solids were removed by centrifugation. Distillation. (35 °C, 0.01 Torr.) yielded a clear mobile oil whose ^{31}P NMR was consistent with literature values.

Methylenetriphenylphosphorane: This phosphorane was synthesized from perprotio materials as described in Chapter 1. The final product was recrystallized from toluene/pentane twice to provide analytically pure, yellow crystals.

Typical NMR experiment. In the drybox the metallacycle was placed in a sealable tared NMR tube. Additional reagents, if solid, were also then introduced at this time. On a high-vacuum line the NMR tube was evacuated, and the the deuterated solvent was condensed into the tube at 77

K. Any volatile reagents were then additionally condensed into the tube from previously tared, evacuated, dried vessels. The tube was sealed under dynamic vacuum with a torch. Dissolution of the materials was achieved at low temperature. NMR spectra were recorded at low temperature, typically -20 °C, before, and at intervals during photolysis. Additionally, the volatile components of each reaction were removed and examined by NMR.

Typical NMR experiment with *in situ* generated (acetylene)titanocene: In a drybox, the metallacycle and deuterated solvent and acetylene were loaded into a septum-capped NMR tube. The stoichiometries were matched as closely as possible. The tube was quickly removed from the drybox and sealed with parafilm™ and placed in a -78 °C dry ice/acetone bath. NMR examination of the reaction mixture prior to photolysis revealed that thermal reactions were not occurring. The NMR tube was photolyzed at -78 °C until no starting metallacycle was observable by NMR. This was typically 1 hour per 10 mgs of neohexene metallacycle. The next reagent, typically a phosphorus ylide (if solid, it was dissolved in a minimum of deuterated solvent), or a ketone, was added by syringe. The reaction was then followed by variable temperature NMR.

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Appendix:

Crystal structure data for μ-(1-3η:2-4η-*trans*, *trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-bis(bis(η^5-cyclopentadienyl)titanium) from the reaction of neohexyne with titanocene.

Crystal Color: green	Formula Weight : 518.46
Habit: prisms	Formula: $Ti_2C_{32}H_{38}$
Temperature 21 °C	MoK α with graphite monochromator
Crystal Size: 0.29x0.25x0.26 mm	Absences: h0l, h+l odd: 0k0, k odd
CAD-4	μ=6.52 cm^{-1} (μr_{max}=0.15)
θ-2θ scan (w scan)	Octants collected: ±h,±k,l

Number of reflections measured: 4941

Number of independent reflections: 2292

Number with $F_o^2>0$: 2055

Number with $F_o^2>3\sigma(F_o^2)$: 1336

Goodness of fit for merging data 0.955

Final R index 0.0785

Final goodness of fit: 1.55

Crystal System: monoclinic	Space Group: $P2_1/n$ # 14n
a: 8.984(1)	α: 90°
b: 15.007(2)	β: 114.57(1)°
c: 10.676(1)	γ: 90°
volume 1309.0(3)Å^3	z: 2

Transmission factors varied from 0.299 to 0.197

The secondary extinction parameter refined to 0.21(11)x10^{-6}

Structure solved by William P. Schaefer

Heavy atom parameters for μ-(1-3η:2-4η-*trans,trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-bis(bis(η^5-cyclopentadienyl)titanium).

x, y, z and $U_{eq}{}^a \times 10^4$

Atom	x	y	z	U_{eq} or B	
Ti	761(.7)	515(.4)	2003(.6)	339(1)	
C1	−510(3)	−375(2)	77(3)	296(8)	
C2	−765(4)	−574(2)	1180(3)	334(8)	
C3	−1777(5)	−1311(2)	1420(4)	447(9)	
C4	−3561(9)	−1077(6)	742(12)	1346(36)	
C5	−1339(13)	−1462(6)	2919(8)	1183(31)	
C6	−1587(13)	−2188(4)	814(13)	1294(35)	
C11	−1034(9)	1197(3)	2862(7)	883(17)	
C12	−1856(5)	1210(3)	1464(7)	768(17)	
C13	−1043(8)	1746(4)	944(5)	773(16)	
C14	283(7)	2080(3)	2028(9)	860(20)	
C15	272(7)	1757(4)	3198(6)	876(18)	
C16	3228(8)	657(5)	4057(7)	1042(24)	
C17	3678(5)	619(5)	3010(7)	882(20)	
C18	3314(6)	−202(5)	2438(5)	787(18)	
C19	2619(6)	−666(3)	3136(8)	855(21)	
C20	2544(7)	−124(6)	4140(6)	1035(23)	
C4A	3255(22)	1553(12)	−85(17)	3.8(5)	*
C5A	663(23)	2098(13)	−2021(22)	4.8(5)	*
C6A	2345(25)	937(14)	−2572(22)	5.0(5)	*

[a] $U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*)(\vec{a}_i \cdot \vec{a}_j)]$

*Isotropic displacement parameter, B

Assigned Hydrogen Parameters.

x, y and $z \times 10^4$

Atom	x	y	z	B
H11	−1341	869	3473	6.9
H12	−2845	890	936	5.8
H13	−1356	1870	−1	6.1
H14	1077	2479	1975	6.5
H15	1039	1904	4111	6.8
H16	3368	1146	4659	7.7
H17	4162	1078	2694	6.5
H18	3508	−416	1685	6.2
H19	2243	−1267	2974	6.6
H20	2065	−267	4764	8.1
H4A	3710	770	−10	7.4
H4B	3630	680	−1470	7.4
H4C	4070	1590	−730	7.4
H5A	2360	1390	−3010	7.4
H5B	700	930	−3370	7.4
H5C	800	1970	−3180	7.4
H6A	2380	2560	−950	7.4
H6B	550	2370	−1330	7.4
H6C	1830	2080	100	7.4
H4AA	2940	1690	590	7.4
H4AB	3960	1010	130	7.4
H4AC	3830	2010	−260	7.4
H5AA	120	2320	−1520	7.4
H5AB	1050	2540	−2460	7.4
H5AC	−370	1830	−2900	7.4
H6AA	3240	460	−1930	7.4
H6AB	1740	780	−3220	7.4
H6AC	3200	1450	−2520	7.4

Bond Distances and Angles

		Distance(Å)			Distance(Å)
Ti	–C1	2.316(3)	C5A	–H5AB	0.96(2)
Ti	–C2	2.079(3)	C5A	–H5AC	1.09(2)
Ti	–CP1	2.104(1)	C6A	–H6AA	1.08(2)
Ti	–CP2	2.094(1)	C6A	–H6AB	0.72(2)
Ti	–C1	2.147(3)	C6A	–H6AC	1.07(2)
C1	–C2	1.324(4)			
C1	–C1	1.502(4)			
C2	–C3	1.519(5)			
C3	–C4	1.501(11)			
C3	–C5	1.497(11)			
C3	–C6	1.508(11)			
C3	–C4A	1.53(2)			
C3	–C5A	1.51(2)			
C3	–C6A	1.62(2)			
C4	–H4A	0.868(10)			
C4	–H4B	1.002(10)			
C4	–H4C	0.892(10)			
C5	–H5A	0.968(10)			
C5	–H5B	0.985(10)			
C5	–H5C	0.883(10)			
C6	–H6A	0.962(11)			
C6	–H6B	0.905(11)			
C6	–H6C	0.922(11)			
C11	–C12	1.362(9)			
C11	–C15	1.364(9)			
C11	–H11	0.946(7)			
C12	–C13	1.352(8)			
C12	–H12	0.960(6)			
C13	–C14	1.365(9)			
C13	–H13	0.946(6)			
C14	–C15	1.344(9)			
C14	–H14	0.951(7)			
C15	–H15	0.956(6)			
C16	–C17	1.339(9)			
C16	–C20	1.343(10)			
C16	–H16	0.949(7)			
C17	–C18	1.354(9)			
C17	–H17	0.948(6)			
C18	–C19	1.348(8)			
C18	–H18	0.947(6)			
C19	–C20	1.370(9)			
C19	–H19	0.953(6)			
C20	–H20	0.956(7)			
C4A	–H4AA	0.90(2)			
C4A	–H4AB	1.00(2)			
C4A	–H4AC	0.92(2)			
C5A	–H5AA	0.92(2)			

Bond Distances and Angles

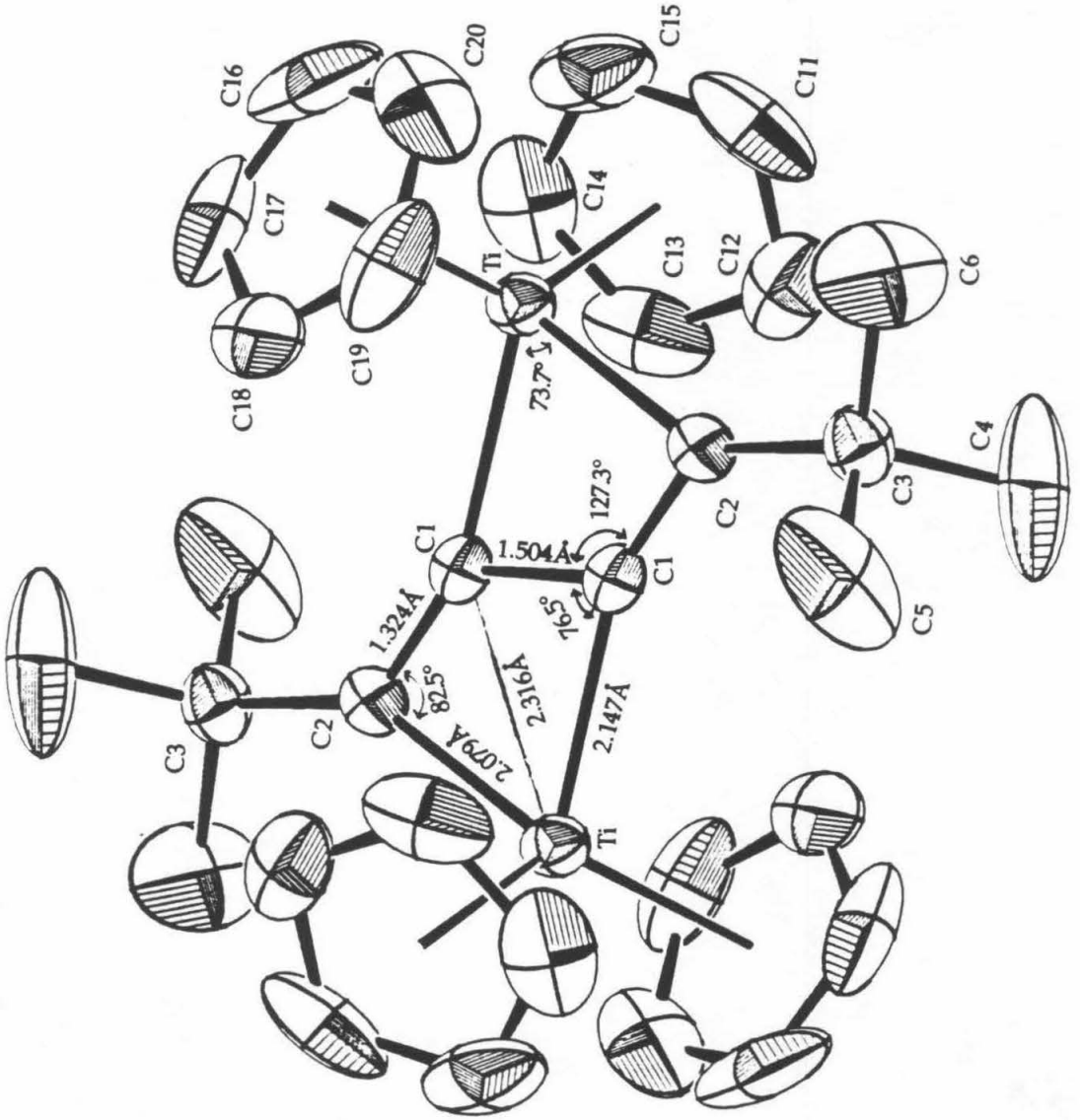
			Angle(°)
CP1	-Ti	-CP2	132.4(0)
C1	-Ti	-C2	34.5(1)
C1	-Ti	-C1	39.10
C1	-C1	-C2	127.3(3)
C3	-C2	-C1	130.7(3)
C4	-C3	-C2	110.1(5)
C5	-C3	-C2	112.4(5)
C6	-C3	-C2	112.4(5)
C4A	-C3	-C2	111.3(7)
C5A	-C3	-C2	107.7(8)
C6A	-C3	-C2	106.1(8)
C5	-C3	-C4	107.7(6)
C6	-C3	-C4	106.6(6)
C6	-C3	-C5	107.4(6)
C5A	-C3	-C4A	112.0(11)
C6A	-C3	-C4A	111.4(11)
C6A	-C3	-C5A	108.2(11)
C15	-C11	-C12	107.2(6)
H11	-C11	-C12	125.6(7)
H11	-C11	-C15	127.2(7)
C13	-C12	-C11	108.6(5)
H12	-C12	-C11	125.7(6)
H12	-C12	-C13	125.7(6)
C14	-C13	-C12	107.5(5)
H13	-C13	-C12	125.7(6)
H13	-C13	-C14	126.9(6)
C15	-C14	-C13	108.4(6)
H14	-C14	-C13	126.3(6)
H14	-C14	-C15	125.3(7)
C14	-C15	-C11	108.4(6)
H15	-C15	-C11	125.9(6)
H15	-C15	-C14	125.7(6)
C20	-C16	-C17	108.9(6)
H16	-C16	-C17	126.6(7)
H16	-C16	-C20	124.5(7)
C18	-C17	-C16	108.4(6)
H17	-C17	-C16	127.6(7)
H17	-C17	-C18	124.1(6)
C19	-C18	-C17	107.5(5)
H18	-C18	-C17	126.6(6)
H18	-C18	-C19	125.8(6)
C20	-C19	-C18	108.1(6)
H19	-C19	-C18	126.8(6)
H19	-C19	-C20	125.1(6)
C19	-C20	-C16	107.1(6)
H20	-C20	-C16	126.3(7)
H20	-C20	-C19	126.5(7)

ATOM	ATOM	DISTANCE
TI	C1	2.3162
TI	C2	2.0795
TI	C1	2.1474
C1	C2	1.3240
C1	C1	1.5021

ATOM	ATOM	ATOM	ANGLE
C2	TI	C1	34.53
C1	TI	C1	39.10
C1	TI	C2	73.63
TI	C1	TI	140.90
C2	C1	TI	62.91
C1	C1	TI	64.37
C2	C1	TI	156.19
C1	C1	TI	76.53
C1	C1	C2	127.28
C1	C2	TI	82.57

Observed and Calculated Structure factors for μ-(1-3η:2-4η-*trans, trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-bis(bis(η^5-cyclopentadienyl)titanium).

The columns contain, in order, k, $10F_{obs}$, $10F_{calc}$ and $10\left(\frac{F^2_{obs}-F^2_{calc}}{\sigma F^2_{obs}}\right)$. A minus sign preceeding F_{obs} indicates that F^2_{obs} is negative.



μ-(1-3η:2-4η-*trans*,*trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-

bis(bis(η^5-cyclopentadienyl)titanium)

-10 k 1

1	95	95	0

-10 k 2

0	62	22	12
1	-19	17	-3
2	53	54	0
3	91	88	2
4	58	40	9

-10 k 3

1	-32	43	-15
2	60	69	-6
3	-49	18	-14
4	114	104	10
5	33	27	1

-10 k 4

0	71	50	9
1	24	4	3
2	87	75	9
3	-31	22	-7
4	60	31	13
5	45	32	5
6	49	45	1

-10 k 5

1	30	48	-8
2	66	63	2
3	-30	15	-6
4	106	108	-2
5	-55	10	-16
6	111	97	13

-10 k 6

0	145	158	-12
1	47	3	11
2	122	124	-2
3	-34	34	-12
4	20	19	0
5	-47	49	-22
6	72	27	24

-10 k 7

1	126	129	-3
2	53	40	6
3	68	117	-41
4	63	67	-2
5	23	20	0

-10 k 8

0	54	54	0
1	-33	10	-6
2	45	26	7
3	64	43	11
4	70	30	21

-9 k 1

0	91	112	-15
1	32	3	6
2	136	136	0
3	51	7	14
4	56	56	0
5	-38	26	-11
6	30	44	-5
7	35	20	4

-9 k 2

1	69	65	2
2	85	70	11
3	72	97	-22
4	178	157	31
5	37	34	1
6	109	99	10
7	-14	8	-1
8	-43	41	-18

-9 k 3

0	169	162	7
1	32	21	3
2	89	100	-10
3	75	82	-5
4	-40	21	-11
5	73	69	3
6	-48	27	-16
7	-15	36	-8
8	65	61	2
9	-16	15	-2

-9 k 4

1	147	149	-1
2	-23	45	-14
3	48	61	-7
4	56	72	-10
5	31	24	2
6	51	61	-6
7	61	61	0
8	44	23	7
9	136	131	5

-9 k 5

0	179	165	14
1	66	44	14
2	88	88	0
3	111	108	3
4	-18	23	-4
5	126	120	7
6	-25	33	-9
7	102	78	22
8	-45	20	-13
9	40	5	8

-9 k 6

1	301	302	-2
2	-29	37	-12
3	124	116	10
4	27	25	0
5	43	54	-5
6	-59	4	-19
7	90	68	17
8	45	33	4
9	155	156	0

-9 k 7

0	94	93	0
1	40	37	1
2	89	97	-7
3	128	123	6
4	46	21	9
5	134	118	20
6	44	17	9
7	99	109	-10
8	58	17	16

-9 k 8

1	132	124	10
2	23	5	2
3	58	78	-15
4	52	44	3
5	-15	12	-2
6	74	82	-6
7	57	52	2

-9 k 9

0	86	68	10
1	9	33	-5
2	55	55	0
3	116	117	0
4	-17	13	-2
5	108	94	14
6	-27	38	-10

-9 k 10

1	49	30	8
2	84	64	15
3	91	82	7
4	147	150	-2

-8 k 1

1	260	270	-18
2	57	47	6
3	156	158	-2
4	78	85	-6
5	36	11	7
6	85	78	5
7	68	41	17
8	26	20	1
9	118	116	2
10	37	3	7

-8 k 2

0	25	30	-1
1	32	25	2
2	14	17	0
3	169	169	0
4	-51	10	-16
5	211	208	5
6	51	32	9
7	108	101	8
8	25	25	0
9	-61	13	-21
10	-45	18	-13
11	40	48	-3

-8 k 3

1	331	331	-1
2	19	10	1
3	129	130	-2
4	-2	61	-21
5	54	78	-18
6	58	38	11
7	108	101	7
8	66	19	24
9	159	149	13
10	27	27	0
11	126	107	22

-8 k 4

0	144	151	-6
1	74	59	12
2	58	51	4
3	158	159	-1
4	128	124	5
5	147	148	-1
6	70	55	10
7	128	138	-13
8	40	29	4
9	-45	26	-14
10	-19	55	-18
11	52	70	-12

-8 k 5

1	235	228	11
2	62	63	0
3	155	162	-10
4	46	60	-8
5	-36	17	-9
6	52	73	-14
7	127	131	-4
8	69	62	5
9	161	165	-5
10	12	6	0
11	92	91	0

-8 k 6

0	290	284	9
1	39	55	-8
2	218	209	15
3	183	182	1
4	-24	28	-8
5	127	132	-7
6	50	60	-6
7	82	68	12
8	97	94	3
9	39	37	0
10	124	124	0
11	27	27	0

-8 k 7

1	18	0	2
2	163	158	7
3	-37	44	-19
4	218	223	-8
5	68	72	-3
6	115	100	16
7	41	26	6
8	110	118	-9
9	-24	0	-3
10	-35	26	-10

-8 k 8

0	58	59	0
1	-29	17	-7
2	106	91	16
3	-31	12	-6
4	63	58	3
5	-68	1	-25
6	87	66	17
7	-23	27	-7
8	74	85	-9
9	14	13	0
10	59	59	0

-8 k 9

1	-37	32	-14
2	121	138	-22
3	45	14	10
4	206	195	18
5	29	39	-3
6	112	113	0
7	-15	51	-15
8	87	87	0

-8 k 10

0	109	97	9
1	-39	27	-13
2	112	105	8
3	113	110	3
4	85	50	25
5	81	107	-24
6	-47	31	-16
7	69	69	0

μ-(1-3η:2-4η-*trans*,*trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-

bis(bis(η^5-cyclopentadienyl)titanium)

	-8 k 11			4	170	162	13	7	51	75	-15	6	122	103	26
				5	90	66	25	8	58	14	17	7	183	175	14
1	85	74	9	6	43	39	2					8	51	35	8
2	26	36	-3	7	66	63	3		-7 k 11			9	-13	7	-1
3	96	108	-11	8	194	193	0					10	95	81	15
4	-37	50	-20	9	46	35	5	0	98	49	29	11	214	226	-21
				10	188	189	0	1	35	40	-2	12	122	151	-39
	-7 k 1			11	48	14	12	2	77	77	0	13	68	83	-12
				12	54	66	-8	3	87	94	-6	14	-42	4	-10
0	238	241	-4	13	56	21	15	4	70	47	15				
1	101	82	21					5	103	90	13		-6 k 5		
2	198	202	-8		-7 k 6			6	34	12	5				
3	185	176	16									1	236	249	-29
4	-24	19	-5	1	108	117	-11		-7 k 12			2	43	45	-1
5	190	191	-1	2	147	146	1					3	237	234	5
6	113	100	15	3	90	97	-6	1	111	107	4	4	72	60	10
7	167	182	-25	4	285	290	-9	2	56	36	9	5	21	44	-9
8	75	69	5	5	27	2	4					6	160	171	-18
9	76	73	2	6	232	239	-15		-6 k 1			7	130	129	0
10	135	128	8	7	92	86	6					8	60	70	-7
11	50	43	4	8	126	141	-20	1	-21	13	-4	9	193	183	16
12	119	108	13	9	119	122	-3	2	216	208	16	10	80	101	-21
				10	23	22	0	3	107	105	3	11	163	158	6
	-7 k 2			11	73	66	5	4	285	272	27	12	67	38	19
				12	98	83	14	5	36	66	-19	13	54	59	-3
1	159	160	-1					6	252	259	-16	14	33	35	0
2	78	76	1		-7 k 7			7	91	87	4				
3	217	216	1					8	232	237	-8		-6 k 6		
4	179	173	11	0	26	72	-19	9	48	81	-24				
5	84	86	-1	1	66	71	-3	10	91	91	0	0	25	10	2
6	177	181	-6	2	57	56	0	11	25	8	3	1	82	85	-2
7	148	147	0	3	276	288	-24	12	54	55	0	2	66	49	13
8	170	167	4	4	40	29	4	13	29	30	0	3	262	265	-4
9	154	145	13	5	191	196	-8	14	131	133	-1	4	65	54	8
10	-51	33	-20	6	16	1	1					5	422	418	8
11	43	36	3	7	70	82	-10		-6 k 2			6	26	35	-3
12	51	17	13	8	45	56	-6					7	286	280	11
13	54	11	15	9	63	76	-9	0	164	176	-17	8	37	39	0
				10	-36	46	-17	1	70	55	13	9	40	49	-4
	-7 k 3			11	79	61	14	2	154	156	-2	10	-52	21	-19
				12	54	51	1	3	161	145	31	11	118	128	-12
0	174	164	12					4	74	87	-13	12	-40	8	-9
1	36	33	1		-7 k 8			5	60	51	6	13	150	139	14
2	182	187	-5					6	134	122	18				
3	130	124	9	1	58	63	-4	7	73	85	-10		-6 k 7		
4	-20	36	-11	2	-27	25	-9	8	239	235	8				
5	108	110	-2	3	85	65	17	9	60	49	7	1	218	225	-13
6	147	153	-9	4	56	62	-4	10	224	218	11	2	87	67	20
7	71	75	-4	5	62	61	1	11	-45	43	-23	3	82	66	16
8	254	247	13	6	120	123	-4	12	70	72	-1	4	242	243	-1
9	67	35	20	7	128	120	10	13	-25	14	-4	5	52	52	0
10	178	189	-17	8	-65	6	-23	14	19	16	0	6	86	86	0
11	41	59	-9	9	105	99	6					7	119	119	0
12	25	17	1	10	22	5	2		-6 k 3			8	5	48	-14
13	99	97	1	11	75	69	4					9	195	199	-6
								1	29	19	3	10	-7	9	0
	-7 k 4				-7 k 9			2	78	80	-2	11	147	143	4
								3	148	156	-14	12	43	74	-19
1	-48	15	-17	0	140	122	19	4	279	272	14	13	68	56	7
2	192	185	13	1	86	69	15	5	40	35	2				
3	99	103	-4	2	-13	12	-2	6	197	201	-8		-6 k 8		
4	254	258	-7	3	196	197	-2	7	141	147	-9				
5	104	87	19	4	57	37	11	8	156	161	-7	0	102	127	-25
6	162	156	9	5	192	201	-17	9	246	237	17	1	43	49	-3
7	30	35	-1	6	-47	5	-13	10	-22	13	-4	2	121	122	0
8	129	132	-5	7	76	77	0	11	68	43	16	3	91	81	10
9	55	18	16	8	48	27	8	12	141	154	-17	4	6	2	0
10	43	49	-3	9	-31	44	-15	13	-49	43	-24	5	189	189	1
11	74	76	-1	10	52	58	-3	14	111	114	-3	6	22	19	0
12	88	66	18									7	134	136	-2
13	-27	6	-4		-7 k 10				-6 k 4			8	37	27	4
												9	50	57	-3
	-7 k 5			1	214	221	-12	0	109	99	10	10	88	81	6
				2	31	12	5	1	-43	13	-15	11	35	34	0
0	164	145	22	3	92	93	0	2	75	84	-10	12	18	38	-6
1	51	29	11	4	-18	37	-9	3	225	230	-10				
2	165	176	-19	5	35	19	4	4	-22	38	-13		-6 k 9		
3	58	58	0	6	26	10	3	5	201	195	11				

μ-(1-3η:2-4η-*trans*,*trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-

bis(bis(η^5-cyclopentadienyl)titanium)

1	197	207	-18	15	34	23	3	1	98	93	6	5	-25	26	-7
2	70	79	-7					2	263	260	6				
3	58	60	-1		-5 k	3		3	51	4	19		-4 k	1	
4	166	159	11					4	40	51	-7				
5	30	10	5	0	117	103	18	5	111	111	0	1	441	439	3
6	98	89	9	1	107	88	29	6	103	105	-1	2	337	315	53
7	98	103	-5	2	171	172	-2	7	29	32	-1	3	216	223	-20
8	55	3	18	3	408	402	12	8	193	194	-1	4	655	656	0
9	109	117	-9	4	184	166	36	9	45	17	11	5	40	49	-6
10	-24	7	-3	5	402	398	8	10	176	180	-7	6	242	234	18
11	126	118	9	6	62	45	13	11	61	45	10	7	192	195	-7
				7	73	77	-3	12	121	121	0	8	162	160	4
	-6 k	10		8	31	36	-2	13	-32	11	-6	9	144	144	0
				9	62	54	6	14	22	29	-1	10	26	23	0
0	321	332	-15	10	28	66	-22					11	211	211	0
1	23	9	2	11	134	147	-18		-5 k	8		12	119	121	-2
2	200	204	-6	12	43	58	-9					13	135	129	8
3	18	26	-2	13	245	244	1	1	57	60	-2	14	133	140	-8
4	35	32	1	14	-45	0	-11	2	67	84	-15	15	64	44	13
5	71	47	16	15	120	131	-14	3	12	12	0	16	118	127	-10
6	-46	37	-21					4	111	92	23				
7	67	51	11		-5 k	4		5	66	61	4		-4 k	2	
8	105	92	13					6	200	196	7				
9	-31	14	-6	1	377	381	-10	7	104	81	26	0	427	408	33
				2	22	34	-6	8	86	88	-2	1	241	247	-15
	-6 k	11		3	202	210	-18	9	-33	39	-15	2	408	415	-15
				4	215	212	7	10	68	81	-11	3	176	186	-26
1	28	12	3	5	-46	31	-23	11	-6	34	-7	4	26	37	-7
2	92	96	-3	6	88	102	-17	12	52	60	-4	5	397	394	7
3	29	9	4	7	-37	28	-15	13	36	5	7	6	-28	21	-11
4	144	130	18	8	155	167	-20					7	42	32	6
5	19	6	1	9	158	141	27		-5 k	9		8	77	73	4
6	108	88	21	10	124	145	-32					9	165	175	-18
7	-33	2	-6	11	239	235	7	0	319	321	-3	10	240	230	21
				12	197	199	-4	1	-37	6	-9	11	-39	20	-12
	-6 k	12		13	140	126	20	2	254	246	15	12	233	233	-1
				14	59	70	-8	3	61	63	-1	13	174	168	9
0	155	153	1	15	27	39	-4	4	152	153	-1	14	41	14	9
1	42	11	9					5	82	70	10	15	54	56	0
2	98	96	2		-5 k	5		6	68	54	9	16	-10	41	-9
3	58	26	15					7	50	15	14				
4	37	2	7	0	298	287	19	8	186	174	20		-4 k	3	
				1	222	225	-6	9	3	26	-3				
	-5 k	1		2	293	300	-17	10	139	131	11	1	221	208	34
				3	280	271	19	11	-15	35	-8	2	386	373	31
0	310	317	-13	4	95	77	22	12	96	97	0	3	159	155	10
1	92	99	-10	5	311	307	9					4	648	648	0
2	-24	27	-11	6	61	35	17		-5 k	10		5	32	54	-17
3	410	406	8	7	164	159	8					6	287	273	32
4	116	124	-13	8	122	129	-10	1	214	212	3	7	168	164	7
5	395	399	-8	9	60	32	17	2	69	47	16	8	88	59	30
6	70	46	19	10	185	195	-19	3	31	39	-3	9	40	54	-8
7	263	256	16	11	32	11	5	4	130	106	30	10	-40	22	-14
8	41	20	8	12	88	100	-12	5	58	51	4	11	-34	30	-14
9	102	108	-7	13	134	144	-14	6	130	126	5	12	209	214	-9
10	58	36	13	14	64	5	24	7	96	87	9	13	52	73	-14
11	77	84	-7	15	86	85	0	8	63	69	-4	14	214	220	-10
12	140	146	-8					9	107	120	-14	15	-28	1	-4
13	136	139	-3		-5 k	6		10	22	22	0	16	133	125	8
14	25	21	1												
15	148	149	0	1	256	255	3		-5 k	11			-4 k	4	
				2	183	182	0								
	-5 k	2		3	86	91	-6	0	32	2	4	0	648	692	-95
				4	356	351	11	1	54	53	0	1	75	47	34
1	380	380	0	5	37	24	5	2	24	65	-20	2	520	523	-6
2	58	51	6	6	406	416	-20	3	162	157	7	3	71	46	27
3	124	126	-3	7	114	124	-14	4	12	60	-19	4	35	65	-27
4	45	21	13	8	134	140	-8	5	139	136	4	5	47	2	21
5	146	133	23	9	149	136	19	6	61	32	16	6	93	94	-1
6	-14	48	-20	10	-10	48	-15	7	86	82	3	7	82	78	4
7	153	151	2	11	95	91	3	8	52	44	4	8	136	142	-11
8	125	133	-12	12	139	116	32					9	-40	14	-12
9	185	164	37	13	54	66	-8		-5 k	12		10	280	264	31
10	68	81	-11	14	123	124	-1					11	42	69	-20
11	247	246	0					1	137	119	23	12	201	208	-12
12	-42	27	-15		-5 k	7		2	31	5	5	13	27	16	2
13	88	64	20					3	68	77	-7	14	-37	54	-24
14	-16	34	-8	0	371	369	2	4	-54	29	-21	15	33	9	6

μ-(1-3η:2-4η-*trans*,*trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-

bis(bis(η^5-cyclopentadienyl)titanium)

16	74	85	-10	4	42	17	10	12	195	194	2	11	213	214	-1
				5	48	33	7	13	96	85	12	12	-41	17	-12
	-4 k	5		6	58	41	10	14	199	192	13	13	16	38	-7
				7	228	223	9	15	-45	7	-13	14	49	36	6
1	49	24	17	8	-17	25	-5	16	77	47	22	15	-18	1	-1
2	452	442	22	9	220	223	-6	17	-22	22	-5				
3	66	62	4	10	43	40	1						-3 k	7	
4	334	341	-16	11	143	120	30		-3 k	3					
5	170	172	-4	12	3	1	0					0	209	214	-8
6	344	351	-14					0	478	476	2	1	147	141	11
7	28	22	2		-4 k	10		1	97	79	34	2	202	199	5
8	192	183	18					2	383	371	29	3	202	215	-30
9	92	68	25	0	102	91	8	3	217	223	-17	4	209	212	-5
10	51	52	0	1	43	70	-19	4	525	496	54	5	177	177	0
11	40	35	2	2	54	50	3	5	443	446	-6	6	73	66	7
12	128	109	25	3	182	183	-2	6	130	121	17	7	137	136	2
13	-16	38	-10	4	29	9	5	7	78	68	12	8	298	297	1
14	154	162	-10	5	253	247	10	8	392	377	31	9	42	45	-1
15	22	29	-2	6	47	68	-14	9	-10	51	-20	10	146	155	-15
				7	166	167	-2	10	134	138	-7	11	42	34	4
	-4 k	6		8	79	91	-11	11	-26	32	-12	12	48	10	14
				9	59	58	0	12	107	108	0	13	129	116	17
0	439	444	-9	10	93	80	12	13	177	178	-1	14	68	33	20
1	106	126	-36					14	32	9	6				
2	225	220	12		-4 k	11		15	98	95	3		-3 k	8	
3	153	159	-12					16	45	26	8				
4	141	144	-4	1	-3	43	-11					1	235	222	27
5	231	247	-36	2	90	80	10		-3 k	4		2	150	150	0
6	94	107	-17	3	74	85	-9					3	79	77	2
7	248	259	-25	4	118	119	-1	1	360	372	-31	4	141	119	34
8	339	317	45	5	51	27	11	2	84	97	-25	5	-31	20	-9
9	79	64	13	6	76	70	4	3	84	91	-11	6	118	104	19
10	203	197	11	7	66	82	-13	4	143	150	-15	7	58	59	0
11	33	44	-5	8	82	70	9	5	223	212	27	8	32	38	-3
12	71	81	-9					6	225	228	-7	9	112	108	5
13	40	37	1		-4 k	12		7	363	367	-7	10	43	64	-14
14	28	43	-6					8	150	151	-1	11	120	121	-1
15	82	72	8	0	100	85	10	9	320	323	-7	12	82	89	-6
				1	26	12	3	10	64	40	17	13	66	55	7
	-4 k	7		2	108	102	7	11	154	148	9				
				3	47	66	-11	12	28	7	5		-3 k	9	
1	253	258	-12	4	27	38	-4	13	45	47	-1				
2	167	165	4	5	110	123	-15	14	89	82	7	0	102	100	1
3	186	190	-8					15	-60	15	-23	1	67	79	-11
4	47	18	13		-3 k	1		16	21	44	-8	2	171	165	9
5	53	26	15									3	165	168	-5
6	42	7	12	0	185	174	23		-3 k	5		4	97	102	-6
7	217	210	13	1	189	193	-12					5	218	220	-3
8	67	61	5	2	424	432	-18	0	268	252	32	6	131	143	-18
9	211	197	24	3	357	339	46	1	271	264	19	7	135	130	6
10	47	20	12	4	303	284	50	2	54	66	-14	8	212	205	12
11	81	71	8	5	337	321	40	3	349	347	4	9	28	26	0
12	18	37	-6	6	171	164	18	4	54	61	-7	10	167	156	17
13	44	66	-13	7	43	42	0	5	262	259	6	11	44	17	9
14	71	62	6	8	296	299	-8	6	53	38	11	12	108	89	20
				9	140	137	4	7	324	301	50				
	-4 k	8		10	218	213	10	8	64	59	4		-3 k	10	
				11	27	25	1	9	185	180	11				
0	84	84	0	12	213	212	2	10	70	93	-23	1	40	14	10
1	88	84	4	13	44	5	12	11	50	23	13	2	141	133	12
2	45	73	-21	14	84	91	-6	12	85	91	-5	3	64	70	-4
3	129	123	10	15	85	86	0	13	125	111	19	4	267	265	3
4	114	108	7	16	49	2	14	14	50	50	0	5	16	31	-4
5	135	133	3	17	63	62	0	15	154	139	21	6	243	247	-9
6	46	45	0					16	47	26	8	7	-23	8	-3
7	158	164	-10		-3 k	2						8	89	99	-10
8	63	64	-1						-3 k	6		9	-42	5	-10
9	39	15	8	1	354	351	7					10	30	14	4
10	69	48	14	2	93	111	-39	1	427	445	-40				
11	80	77	2	3	192	193	0	2	211	205	13		-3 k	11	
12	10	12	0	4	115	129	-34	3	92	108	-26				
13	117	82	38	5	452	428	50	4	66	63	3	0	136	117	19
				6	551	559	-15	5	53	49	3	1	51	10	15
	-4 k	9		7	130	112	34	6	52	68	-13	2	129	124	6
				8	62	54	7	7	262	267	-12	3	57	21	17
1	217	210	12	9	-34	16	-10	8	125	117	11	4	41	48	-3
2	46	39	3	10	29	45	-8	9	358	366	-16	5	43	28	6
3	215	214	2	11	164	173	-18	10	-46	16	-16	6	52	40	6

μ-(1-3η:2-4η-*trans*,*trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-

bis(bis(η5-cyclopentadienyl)titanium)

7	-46	7	-12	4	74	99	-46	7	38	18	7								
8	114	61	36	5	459	474	-33	8	98	102	-5	1	1152	1169	-17				
				6	90	110	-34	9	-29	26	-9	2	290	281	27				
	-3 k	12		7	355	358	-7	10	162	159	5	3	508	500	16				
				8	317	322	-12	11	-48	13	-14	4	289	317	-85				
1	66	66	0	9	100	73	31	12	135	135	0	5	197	198	-2				
2	70	52	12	10	228	233	-9	13	60	28	15	6	372	389	-43				
3	23	44	-7	11	35	10	7					7	207	209	-5				
4	131	115	19	12	-24	10	-4		-2 k	9		8	150	160	-24				
5	-46	10	-12	13	79	90	-11					9	84	85	-1				
				14	26	27	0	1	88	98	-11	10	112	117	-7				
	-2 k	1		15	101	81	18	2	169	170	-1	11	144	148	-7				
				16	-21	42	-12	3	113	109	4	12	118	121	-4				
1	158	143	53					4	270	262	14	13	10	45	-12				
2	527	516	22		-2 k	5		5	-33	19	-9	14	165	152	22				
3	945	909	42					6	251	242	16	15	122	113	12				
4	327	321	16	1	261	269	-22	7	51	34	9	16	113	91	24				
5	307	286	55	2	288	293	-13	8	111	90	24	17	70	85	-11				
6	36	15	13	3	39	37	2	9	59	34	14								
7	521	489	60	4	302	304	-3	10	46	1	13		-1 k	3					
8	101	101	0	5	192	191	2	11	67	75	-5								
9	441	445	-10	6	299	304	-13	12	64	60	2	0	926	956	-31				
10	62	65	-3	7	202	188	31					1	143	132	32				
11	213	204	17	8	207	220	-28		-2 k	10		2	304	300	11				
12	42	36	3	9	116	107	12					3	136	142	-18				
13	112	130	-25	10	30	1	6	0	160	157	3	4	168	171	-10				
14	45	39	3	11	250	243	15	1	-27	28	-10	5	241	238	7				
15	54	20	17	12	76	77	-1	2	53	55	-1	6	385	378	15				
16	35	1	7	13	82	90	-7	3	160	146	21	7	87	87	0				
17	29	41	-4	14	144	138	8	4	-17	7	-2	8	400	398	5				
				15	-21	51	-17	5	238	234	8	9	-17	28	-8				
	-2 k	2		16	112	116	-4	6	29	10	4	10	330	327	5				
								7	126	114	14	11	49	52	-2				
0	198	207	-24		-2 k	6		8	64	70	-4	12	241	240	1				
1	373	372	3					9	56	31	13	13	60	49	9				
2	698	672	40	0	900	905	-5	10	76	53	16	14	66	73	-5				
3	148	166	-53	1	53	55	-1					15	62	30	19				
4	109	120	-26	2	443	440	7		-2 k	11		16	118	120	-2				
5	346	372	-72	3	26	29	-1					17	-26	40	-12				
6	331	324	18	4	88	88	0	1	183	176	11								
7	383	395	-27	5	214	224	-25	2	41	44	-1		-1 k	4					
8	-42	2	-16	6	48	63	-13	3	141	125	22								
9	56	31	18	7	61	66	-4	4	37	6	7	1	340	343	-7				
10	57	38	13	8	222	230	-18	5	33	9	6	2	239	259	-62				
11	97	89	10	9	16	15	0	6	-33	12	-7	3	59	47	14				
12	38	54	-9	10	328	325	5	7	66	50	10	4	488	513	-54				
13	201	199	2	11	31	23	2	8	-21	21	-5	5	122	119	7				
14	31	39	-3	12	202	198	7					6	534	540	-12				
15	105	105	0	13	78	81	-2		-2 k	12		7	64	74	-12				
16	26	25	0	14	-17	29	-6					8	187	191	-8				
17	79	72	5	15	50	11	14	0	50	26	8	9	64	57	6				
								1	48	47	0	10	-26	13	-6				
	-2 k	3			-2 k	7		2	-4	20	-2	11	37	45	-4				
								3	93	95	-1	12	168	171	-5				
1	408	407	2	1	27	42	-8	4	42	36	2	13	55	40	8				
2	57	43	17	2	249	241	19					14	187	178	16				
3	256	263	-19	3	48	61	-11		-1 k	1		15	28	22	2				
4	102	104	-4	4	321	330	-19					16	124	118	6				
5	144	125	48	5	74	62	12	0	1001	1019	-18								
6	42	51	-8	6	297	288	19	1	283	289	-24		-1 k	5					
7	643	633	16	7	53	70	-14	2	1096	1089	6								
8	-28	7	-7	8	59	61	-1	3	224	218	22	0	479	492	-22				
9	443	440	6	9	93	94	-1	4	965	947	21	1	88	98	-19				
10	-40	4	-12	10	66	68	-1	5	39	59	-23	2	574	567	16				
11	275	276	-3	11	-45	0	-12	6	249	229	56	3	145	170	-64				
12	114	99	19	12	165	170	-6	7	326	331	-14	4	299	305	-15				
13	-31	11	-7	13	55	10	19	8	643	637	9	5	154	159	-10				
14	69	65	2	14	156	165	-13	9	70	57	14	6	138	144	-12				
15	100	104	-5					10	375	368	16	7	163	172	-18				
16	-27	23	-7		-2 k	8		11	22	8	2	8	156	160	-8				
17	101	99	1					12	164	170	-11	9	-27	0	-5				
				0	371	365	8	13	25	58	-17	10	234	228	12				
	-2 k	4		1	24	23	0	14	16	7	1	11	62	76	-12				
				2	185	181	8	15	145	142	3	12	251	261	-21				
0	438	434	8	3	23	8	3	16	25	44	-8	13	-3	53	-17				
1	-14	22	-8	4	27	55	-15	17	71	62	6	14	31	34	-1				
2	130	139	-22	5	49	5	16					15	58	59	0				
3	217	217	1	6	64	83	-18		-1 k	2		16	48	23	10				

μ-(1-3η:2-4η-*trans*,*trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-

bis(bis(η^5-cyclopentadienyl)titanium)

	-1 k 6		
1	530	522	15
2	199	196	7
3	115	108	11
4	387	393	-13
5	47	47	0
6	281	277	9
7	57	51	5
8	41	47	-3
9	174	162	20
10	60	44	11
11	215	220	-8
12	181	189	-13
13	113	108	6
14	140	150	-14
15	36	12	6

	-1 k 7		
0	84	72	10
1	74	86	-13
2	117	129	-19
3	216	207	18
4	139	125	23
5	282	289	-16
6	34	12	7
7	128	112	22
8	89	85	5
9	0	17	-2
10	46	54	-5
11	81	73	7
12	47	25	9
13	138	131	9
14	-66	7	-24

	-1 k 8		
1	201	202	-2
2	108	104	6
3	32	16	5
4	39	40	0
5	49	27	11
6	70	33	27
7	52	55	-2
8	73	74	0
9	126	101	33
10	33	27	2
11	135	117	22
12	-8	34	-7
13	79	61	14

	-1 k 9		
0	-29	19	-5
1	93	119	-32
2	21	36	-5
3	227	217	21
4	37	36	0
5	245	233	23
6	54	37	9
7	201	195	9
8	54	48	3
9	27	63	-19
10	-36	8	-7
11	63	36	15

	-1 k 10		
1	243	233	18
2	70	75	-4
3	135	125	14
4	166	159	10
5	68	67	0
6	123	121	2
7	89	91	-2
8	-1	34	-6

	-1 k 11		
0	77	101	-16
1	21	42	-7
2	99	87	13
3	58	61	-2
4	53	16	15
5	76	49	19
6	60	68	-6
7	8	37	-7

	0 k 0		
2	1130	1144	-12
4	164	162	5
6	267	270	-7
8	553	561	-15
10	436	442	-12
12	384	393	-18
14	-22	9	-3
16	90	111	-22

	0 k 1		
1	487	486	1
2	542	535	15
3	310	309	1
4	273	269	12
5	76	62	23
6	443	453	-22
7	116	134	-41
8	100	107	-11
9	85	98	-20
10	89	79	11
11	219	215	9
12	102	82	24
13	104	113	-11
14	219	229	-18
15	57	17	18
16	153	154	-1
17	12	21	-1

	0 k 2		
0	1148	1166	-15
1	107	106	5
2	391	398	-19
3	52	40	14
4	83	86	-4
5	132	137	-11
6	248	261	-38
7	257	247	27
8	286	284	5
9	-20	31	-11
10	201	202	-1
11	20	21	0
12	186	176	17
13	70	59	9
14	33	34	0
15	102	85	17
16	103	110	-8
17	18	59	-17

	0 k 3		
1	205	201	11
2	233	227	19
3	283	288	-14
4	395	383	28
5	-5	4	0
6	318	331	-33
7	189	196	-18
8	-25	37	-17
9	91	100	-13
10	95	95	0
11	243	243	0

	0 k 4		
0	76	70	7
1	214	226	-39
2	200	209	-26
3	443	448	-12
4	239	217	58
5	605	600	8
6	53	46	5
7	233	221	28
8	64	64	0
9	35	46	-7
10	56	43	8
11	96	86	11
12	91	90	0
13	242	238	8
14	69	68	0
15	122	123	-1
16	21	59	-16

	0 k 5		
1	359	363	-9
2	-10	14	-3
3	540	538	4
4	54	70	-17
5	140	135	9
6	47	24	14
7	227	231	-8
8	-8	15	-2
9	204	208	-7
10	55	3	21
11	249	238	22
12	42	53	-6
13	122	126	-4
14	36	59	-13
15	-32	24	-9
16	-39	6	-8

	0 k 6		
0	83	105	-23
1	132	144	-24
2	-18	19	-6
3	345	345	-1
4	65	80	-15
5	371	364	15
6	52	63	-8
7	183	179	8
8	70	74	-3
9	-58	35	-29
10	125	124	1
11	140	156	-24
12	87	96	-9
13	186	193	-11
14	39	20	6
15	107	102	5

	0 k 7		
1	44	31	7
2	135	134	1
3	129	117	18
4	220	215	10
5	70	40	24
6	177	187	-18
7	170	170	0
8	95	88	8
9	156	153	4
10	34	1	7
11	51	53	-1

	0 k 8		
0	78	89	-9
1	94	92	2
2	102	81	25
3	96	109	-16
4	42	46	-2
5	64	69	-4
6	19	51	-14
7	152	150	3
8	142	144	-4
9	62	72	-7
10	99	86	13
11	51	29	10
12	50	35	7

	0 k 9		
1	150	130	31
2	213	209	7
3	86	69	16
4	213	214	-2
5	46	63	-11
6	213	213	0
7	10	45	-11
8	130	126	5
9	106	113	-7
10	-36	23	-10
11	52	59	-3

	0 k 10		
0	259	264	-6
1	-20	13	-3
2	174	160	21
3	12	39	-8
4	40	69	-18
5	10	26	-3
6	81	63	14
7	-40	2	-9
8	180	194	-23

	0 k 11		
1	51	14	14
2	76	70	4
3	52	14	14
4	110	104	6
5	52	0	16

	1 k 0		
1	1169	1152	17
2	572	561	21
3	377	362	45
4	245	242	9
5	345	341	10
6	332	314	57
7	359	354	17
8	35	38	-2
9	369	373	-12
10	-26	4	-7
11	365	371	-15
12	170	182	-30
13	198	203	-14
14	123	126	-6
15	-11	29	-9
16	51	48	2
17	105	85	28

	1 k 1		
0	438	437	1
2	451	452	-1

μ-(1-3η:2-4η-*trans*,*trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-

bis(bis(η^5-cyclopentadienyl)titanium)

3	373	379	-16	1	107	116	-17
4	331	352	-61	2	243	249	-15
5	485	500	-32	3	213	221	-19
6	17	2	3	4	200	192	17
7	393	407	-34	5	179	183	-9
8	169	176	-17	6	230	229	3
9	106	103	3	7	93	104	-13
10	62	8	30	8	294	288	14
11	37	19	8	9	41	1	11
12	124	123	1	10	192	194	-4
13	219	221	-4	11	63	64	0
14	36	36	0	12	147	145	3
15	171	171	0	13	99	91	8
16	-47	15	-16	14	21	42	-7
17	112	105	7	15	82	74	7

1 k 2

1	211	196	46	1	-37	24	-15
2	251	246	16	2	250	260	-22
3	95	71	46	3	86	75	13
4	251	252	0	4	321	325	-10
5	22	25	-2	5	67	72	-5
6	93	103	-14	6	305	298	15
7	192	197	-12	7	23	8	3
8	17	26	-3	8	215	222	-15
9	218	215	7	9	-31	22	-10
10	-22	19	-6	10	-51	7	-17
11	172	177	-9	11	-29	23	-9
12	57	33	14	12	160	151	13
13	93	101	-9	13	-46	6	-13
14	36	12	7	14	147	133	18
15	6	35	-7				
16	36	12	7				
17	60	56	2				

1 k 3

0	82	78	4
1	177	184	-21
2	229	227	6
3	493	481	25
4	88	97	-17
5	678	691	-20
6	230	224	17
7	253	261	-21
8	122	119	4
9	83	81	2
10	74	77	-3
11	86	90	-4
12	79	75	4
13	280	278	3
14	57	53	2
15	144	154	-15
16	52	55	-2

1 k 4

1	382	386	-11
2	148	146	4
3	258	269	-29
4	484	495	-21
5	128	111	32
6	338	341	-7
7	124	124	0
8	-25	32	-12
9	150	146	7
10	-26	11	-5
11	152	154	-3
12	179	168	18
13	111	113	-3
14	120	135	-20
15	53	46	4
16	64	46	11

1 k 5

0	118	122	-6

1 k 6

0	221	224	-4
1	70	80	-10
2	146	134	21
3	111	115	-4
4	55	44	7
5	26	67	-24
6	118	122	-6
7	85	82	3
8	254	254	0
9	-29	24	-9
10	186	180	9
11	79	76	2
12	58	50	4
13	60	66	-4

1 k 7

1	90	74	17
2	169	146	38
3	-26	39	-14
4	166	173	-12
5	51	54	-2
6	220	219	0
7	78	72	6
8	135	141	-7
9	85	72	11
10	-32	7	-6
11	10	18	-1

1 k 8

0	286	289	-3
1	87	70	16
2	197	188	15
3	80	98	-18
4	41	45	-2
5	93	90	3
6	55	63	-5
7	89	89	0
8	153	151	2
9	65	2	25

1 k 9

1	154	156	-3
2	58	34	13
3	58	71	-8
4	51	54	-2
5	28	10	3
6	66	65	0
7	92	99	-6

2 k 0

0	40	50	-14
1	159	157	7
2	223	215	35
3	37	8	23
4	314	310	12
5	713	691	36
6	38	42	-5
7	472	470	5
8	399	403	-11
9	170	168	6
10	207	198	26
11	71	76	-7
12	162	167	-10
13	250	255	-14
14	51	78	-29
15	125	115	18
16	25	0	5
17	101	89	16

2 k 1

1	702	673	44
2	648	642	8
3	171	151	55
4	690	673	25
5	31	0	11
6	681	666	30
7	61	84	-32
8	164	168	-10
9	126	115	19
10	32	64	-22
11	58	34	15
12	197	199	-4
13	46	32	7
14	206	216	-19
15	-13	0	-1
16	85	63	17
17	18	19	0

2 k 2

0	409	452	-90
1	264	262	6
2	300	303	-10
3	238	229	26
4	168	172	-9
5	84	81	6
6	179	199	-53
7	223	221	5
8	319	324	-11
9	26	51	-14
10	173	175	-3
11	102	114	-15
12	112	123	-16
13	41	39	1
14	37	21	5
15	65	52	8
16	5	38	-8

2 k 3

1	57	52	5
2	571	582	-19
3	144	132	26
4	649	659	-17
5	41	45	-3
6	423	423	0

2 k 4

0	601	619	-26
1	68	63	6
2	364	366	-4
3	38	31	4
4	95	95	0
5	114	96	29
6	129	136	-12
7	-44	5	-15
8	265	260	11
9	61	69	-7
10	284	284	0
11	19	17	0
12	201	206	-9
13	89	105	-16
14	38	34	1
15	-33	30	-11

2 k 5

1	184	184	0
2	176	183	-15
3	203	204	-1
4	270	272	-3
5	60	36	16
6	249	248	2
7	136	124	19
8	102	94	9
9	129	121	12
10	30	20	3
11	128	125	4
12	61	32	16
13	68	49	12
14	98	114	-17

2 k 6

0	222	221	1
1	112	97	19
2	86	82	3
3	211	216	-10
4	106	110	-5
5	254	252	4
6	117	117	0
7	207	216	-17
8	120	115	5
9	60	72	-10
10	165	163	3
11	73	60	10
12	96	106	-11
13	108	107	1

2 k 7

1	326	336	-21
2	40	0	11
3	110	103	9
4	91	94	-3
5	-37	2	-9
6	87	78	9
7	95	101	-6
8	-40	19	-12
9	184	164	32
10	41	47	-3
11	113	104	10
12	31	16	4

μ-(1-3η:2-4η-*trans*,*trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-

bis(bis(η5-cyclopentadienyl)titanium)

	2 k 8			4	364	358	12	10	13	44	-10	0	23	11	2
				5	121	127	-11	11	137	127	13	1	38	69	-29
				6	357	355	4	12	47	32	6	2	137	143	-11
0	95	55	26	7	169	161	15					3	16	41	-12
1	75	66	8	8	136	138	-3		3 k 7			4	152	154	-2
2	95	102	-7	9	110	125	-20					5	89	91	-2
3	132	109	33	10	187	182	10	0	195	194	0	6	43	7	13
4	-20	19	-5	11	136	137	-1	1	49	21	13	7	205	192	25
5	150	140	15	12	128	133	-7	2	106	88	21	8	52	47	3
6	38	48	-5	13	50	32	9	3	102	105	-4	9	25	41	-7
7	115	114	2	14	103	107	-4	4	37	12	8	10	-11	15	-2
8	26	6	3	15	52	61	-6	5	130	122	10	11	84	93	-10
9	-5	11	-1	16	95	87	7	6	52	31	11	12	84	66	15
10	48	44	2					7	46	23	9	13	107	82	26
					3 k 3			8	77	70	6	14	31	21	3
	2 k 9							9	-28	3	-4	15	125	124	2
				0	652	650	3	10	81	76	4				
1	225	227	-3	1	99	112	-16						4 k 3		
2	-44	2	-11	2	330	341	-19		3 k 8						
3	113	113	0	3	138	151	-26					1	363	380	-37
4	-48	20	-16	4	-35	26	-16	1	113	115	-1	2	78	60	17
5	-21	5	-3	5	165	172	-15	2	54	59	-3	3	237	245	-18
6	30	24	1	6	-57	6	-25	3	124	129	-5	4	100	90	12
7	108	88	20	7	122	122	0	4	84	69	13	5	78	66	12
8	-37	17	-9	8	180	190	-21	5	52	22	14	6	173	166	13
				9	-19	30	-8	6	83	80	3	7	207	190	32
	2 k 10			10	198	198	0	7	40	18	7	8	52	63	-7
				11	60	73	-9	8	-44	15	-12	9	270	282	-24
0	156	144	11	12	69	78	-6					10	44	12	12
1	52	26	11	13	176	157	30		3 k 9			11	142	132	15
2	115	103	11	14	41	50	-4					12	76	59	12
3	91	65	23	15	127	123	4	0	167	165	2	13	98	81	16
4	58	45	7					1	-63	10	-22	14	74	77	-2
					3 k 4			2	137	130	9				
	3 k 0							3	36	33	1		4 k 4		
				1	500	501	-2	4	39	50	-5				
1	465	451	32	2	28	27	0	5	18	15	0	0	339	338	2
2	720	696	41	3	122	123	-3					1	4	33	-7
3	403	393	25	4	25	23	0		4 k 0			2	210	214	-8
4	880	849	41	5	-32	24	-11					3	20	10	2
5	220	204	55	6	80	80	0	0	356	357	-3	4	48	1	16
6	771	771	0	7	115	110	5	1	294	308	-46	5	56	51	3
7	263	260	11	8	58	56	0	2	130	128	4	6	111	114	-2
8	238	226	37	9	245	238	15	3	522	512	22	7	134	132	2
9	186	189	-9	10	33	13	6	4	140	136	11	8	152	166	-23
10	24	37	-8	11	254	256	-3	5	575	579	-8	9	87	80	6
11	42	5	17	12	-11	24	-4	6	93	87	10	10	169	157	20
12	251	248	8	13	122	114	9	7	360	361	-3	11	49	14	13
13	-20	26	-10	14	46	8	12	8	43	51	-7	12	117	112	5
14	221	223	-5					9	-27	36	-20	13	53	39	7
15	36	15	9		3 k 5			10	141	137	8				
16	133	140	-12					11	122	114	15		4 k 5		
				0	160	152	10	12	28	31	-1				
	3 k 1			1	54	72	-15	13	172	174	-5	1	65	42	17
				2	65	56	7	14	-33	8	-10	2	183	185	-3
0	432	431	1	3	167	168	-2	15	161	167	-14	3	116	117	0
1	253	227	73	4	36	2	9	16	41	45	-2	4	277	268	18
2	187	188	-2	5	269	276	-14					5	40	19	8
3	276	271	9	6	64	61	2		4 k 1			6	244	246	-2
4	-16	26	-9	7	198	199	-2					7	102	106	-4
5	323	309	34	8	27	56	-15	1	739	748	-12	8	116	106	12
6	124	125	-2	9	88	74	14	2	70	72	-2	9	61	82	-17
7	140	150	-14	10	-42	26	-15	3	178	180	-4	10	32	15	4
8	238	218	44	11	34	12	6	4	100	112	-20	11	23	13	2
9	38	53	-10	12	33	34	0	5	-25	20	-8	12	91	73	15
10	206	202	8	13	117	95	23	6	15	18	0				
11	31	45	-6					7	143	136	12		4 k 6		
12	140	147	-11		3 k 6			8	78	79	-1				
13	189	186	5					9	243	249	-12	0	164	180	-18
14	46	0	14	1	311	307	8	10	96	106	-11	1	26	24	0
15	36	58	-11	2	93	100	-8	11	222	212	18	2	192	203	-20
16	79	65	11	3	172	183	-20	12	9	2	0	3	-27	1	-4
				4	127	125	3	13	87	69	16	4	101	88	15
	3 k 2			5	43	45	-1	14	17	3	1	5	62	2	25
				6	130	124	7	15	14	41	-8	6	115	109	7
1	379	389	-24	7	146	138	11					7	31	27	1
2	471	468	6	8	17	27	-2		4 k 2			8	160	153	10
3	322	310	23	9	143	142	0					9	-54	4	-17

μ-(1-3η:2-4η-*trans*,*trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-

bis(bis(η^5-cyclopentadienyl)titanium)

10	122	125	-2	0	235	221	20	12	113	94	28	1	-10	26	-4
11	26	31	-1	1	88	91	-4	13	66	43	19	2	91	100	-9
				2	194	191	3	14	34	46	-7	3	85	94	-8
	4 k	7		3	115	103	15					4	-26	44	-14
				4	103	100	3		6 k	1		5	91	101	-9
1	-25	16	-5	5	113	103	13								
2	73	74	0	6	167	157	16	1	160	148	21		7 k	0	
3	-33	25	-10	7	55	61	-4	2	8	37	-8				
4	143	149	-7	8	324	325	-2	3	89	105	-18	1	362	367	-13
5	24	35	-3	9	35	44	-4	4	135	109	36	2	53	53	0
6	75	83	-7	10	200	200	0	5	67	53	10	3	190	189	3
7	84	64	16	11	72	50	15	6	104	76	31	4	73	68	7
8	25	16	2	12	94	89	5	7	177	169	14	5	49	34	11
				13	-30	32	-10	8	68	72	-3	6	-44	2	-18
	4 k	8						9	198	198	1	7	168	177	-21
					5 k	4		10	24	17	1	8	22	4	4
0	73	62	5					11	78	51	20	9	170	179	-19
1	-19	31	-7	1	113	106	9	12	70	55	10	10	12	3	1
2	87	88	0	2	187	203	-29	13	18	38	-6	11	145	142	4
3	78	60	14	3	127	132	-7					12	53	22	17
4	-45	48	-24	4	308	306	4		6 k	2					
5	81	73	6	5	37	28	3						7 k	1	
				6	273	273	0	0	176	184	-11				
	5 k	0		7	114	100	18	1	128	135	-11	0	82	93	-7
				8	135	138	-4	2	98	85	15	1	57	62	-3
1	343	341	4	9	84	93	-8	3	212	216	-8	2	42	55	-7
2	101	103	-5	10	-49	11	-14	4	66	70	-3	3	223	224	0
3	276	273	10	11	48	49	0	5	209	203	11	4	63	80	-14
4	158	164	-16	12	52	74	-14	6	127	135	-12	5	241	230	21
5	45	40	4					7	139	140	0	6	-43	30	-16
6	333	327	17		5 k	5		8	113	115	-2	7	120	98	26
7	199	198	2					9	21	25	-1	8	34	66	-17
8	184	177	17	0	127	120	6	10	105	103	1	9	24	6	3
9	297	301	-11	1	35	41	-2	11	51	68	-11	10	27	13	3
10	45	41	3	2	117	111	7	12	35	71	-20	11	90	85	4
11	127	125	4	3	138	125	18								
12	27	11	5	4	48	38	5		6 k	3			7 k	2	
13	33	29	2	5	169	167	2								
14	111	106	8	6	92	68	23	1	220	222	-3	1	187	189	-3
15	-18	3	-2	7	103	101	2	2	137	133	5	2	21	18	0
				8	90	101	-11	3	145	138	10	3	70	51	14
	5 k	1		9	60	48	7	4	217	225	-14	4	35	45	-4
				10	86	92	-6	5	62	23	21	5	27	41	-5
0	344	335	16					6	164	160	6	6	54	17	16
1	-51	10	-21		5 k	6		7	146	135	15	7	52	48	2
2	136	144	-14					8	89	102	-12	8	33	27	1
3	18	9	1	1	88	75	12	9	151	159	-12	9	68	72	-3
4	-40	17	-14	2	84	72	11	10	18	16	0	10	-33	13	-7
5	90	80	10	3	90	109	-20	11	111	102	9				
6	31	44	-6	4	103	118	-17						7 k	3	
7	57	65	-5	5	-30	8	-5		6 k	4					
8	232	237	-9	6	60	63	-2					0	142	149	-7
9	21	11	2	7	117	107	10	0	-72	47	-32	1	87	84	2
10	214	210	9	8	59	13	19	1	62	83	-17	2	102	101	0
11	-38	11	-9					2	-24	31	-10	3	203	211	-14
12	81	87	-5		5 k	7		3	219	226	-12	4	60	48	7
13	60	27	17					4	88	93	-5	5	200	207	-12
14	-21	27	-6	0	-44	10	-8	5	249	254	-10	6	53	10	16
				1	60	38	12	6	-9	28	-4	7	138	141	-4
	5 k	2		2	40	11	8	7	163	164	-2	8	55	24	13
				3	115	118	-3	8	-14	16	-2	9	4	36	-6
1	58	63	-4	4	-12	12	-1	9	52	48	2				
2	164	171	-13	5	116	127	-12	10	40	4	9		7 k	4	
3	169	170	-1												
4	113	92	25		6 k	0			6 k	5		1	61	67	-3
5	77	74	3									2	75	54	16
6	195	191	8	0	267	272	-9	1	140	124	22	3	-35	27	-11
7	38	56	-10	1	150	157	-15	2	20	29	-2	4	95	91	3
8	94	96	-1	2	297	291	16	3	73	78	-3	5	14	45	-9
9	78	71	6	3	171	178	-16	4	-21	4	-2	6	102	78	21
10	-35	37	-16	4	164	170	-15	5	71	7	30				
11	-13	21	-4	5	166	170	-10	6	-50	6	-14		7 k	5	
12	70	47	14	6	136	142	-11	7	54	28	12				
13	-34	24	-10	7	144	150	-14	8	44	18	9	0	173	176	-3
14	95	94	1	8	306	312	-15					1	-40	2	-8
				9	-44	6	-18		6 k	6		2	119	121	-1
	5 k	3		10	217	214	7					3	63	9	21
				11	-28	2	-7	0	72	82	-5				

μ-(1-3η:2-4η-*trans,trans*-1,4-di-*tert*-Butyl-1,3-butadiene)-

bis(bis(η^5-cyclopentadienyl)titanium)

	8	k	0		1	48	20	11	5	74	75	0	4	140	145	-9
					2	63	79	-11	6	18	9	1	5	-40	5	-12
0	210	214	-7		3	41	35	2	7	23	46	-8	6	127	119	13
1	49	29	13		4	125	129	-5								
2	138	138	1		5	52	6	16		8	k	3		9	k	1
3	146	149	-6		6	85	83	1								
4	-32	33	-17		7	-30	2	-5	1	48	52	-1	0	47	24	6
5	144	139	10		8	41	29	5	2	71	69	1	1	-36	18	-8
6	39	28	6						3	-47	29	-16	2	20	26	-1
7	43	30	7			8	k	2	4	111	106	4	3	52	66	-8
8	91	76	18										4	-62	34	-26
9	-23	28	-10		0	116	109	5		9	k	0				
10	127	129	-2		1	20	15	1						1	k	1
					2	93	82	10	1	94	101	-9				
	8	k	1		3	83	60	18	2	61	68	-6	1	15	606	--
					4	44	38	2	3	23	45	-11				

CHAPTER 3

Investigations of Possible Photochemical Routes to α-Oxatitanacyclobutanes

Introduction:

During the course of our investigations into the reactivity of titanocene, we investigated the reaction of titanocene with epoxides and episulfides. This investigation was undertaken for a number of reasons. First, it was noticed that the stoichiometry of a molecule of an epoxide and a molecule of titanocene was identical to that of an α-oxabis(cyclopentadienyl)titanacyclobutane, also termed 1,2-metallaoxetanes.

Figure 1. Possible reaction between titanocene and an epoxide.

If reaction of titanocene and an epoxide furnished a route to oxatitanacyclobutanes, Figure 1, then many questions about the nature of these important intermediates could be addressed. Second, the photochemical generation of titanocene lends itself to the investigation of reactive intermediates, since titanocene can be generated cleanly at low temperatures. It was felt (and later successfully realized) that this investigation could provide information about the nature of photochemically generated titanocene. Unfortunately, the characterization of oxatitanacyclobutanes was not achieved. Third, epoxides are of considerable synthetic utility, and an understanding of their reactivity with transitions metals is important to developing new reactions and organic

transformations. Epoxides are capable of reacting with transition-metal complexes to afford interesting and useful synthetic transformations.[1]

Oxametallacyclobutanes often have been postulated as intermediates in many organic reactions such as olefin oxidations, organic deoxygenations, and alkylidene transfer reactions.[2] However, they have rarely been observed in the systems in which they are invoked. This paucity of examples has cast doubt on their intermediacy in these reactions. Recently, there has been a resurgence in the number of investigations into oxametallacyclobutanes, and the number of isolated α-oxametallacyclobutanes has increased markedly.[3] Notably, there are still very few examples of early metal oxatitanacyclobutanes, yet many of the transformations that may involve the intermediacy of α-oxametallacyclobutanes are reactions involving early metals.

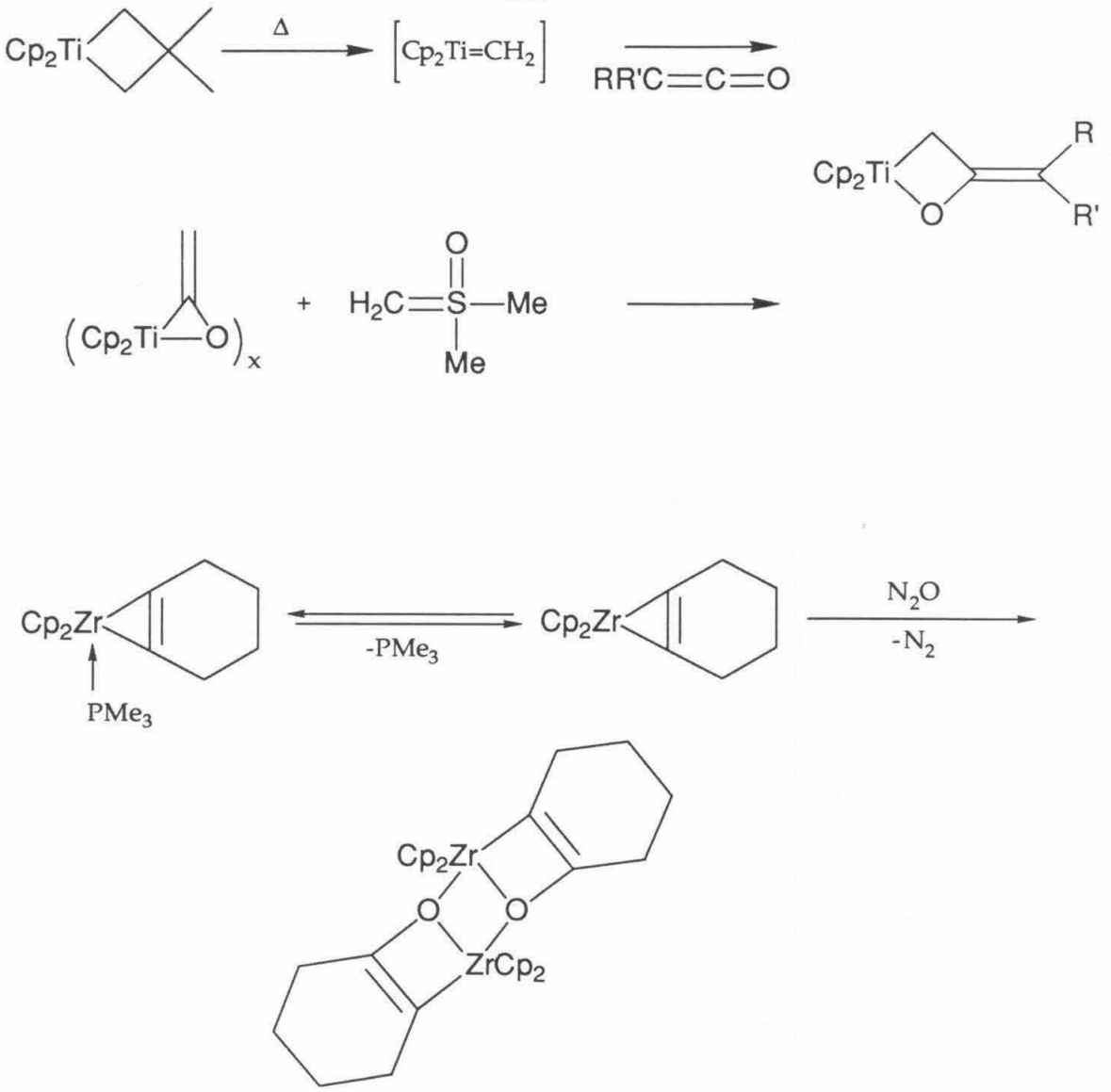


Figure 2. Examples of early metal α-oxametalacyclobutanes.

Early metal containing oxametallacyclobutanes[4] and oxametallacyclobutenes[5] are shown in Figure 2, along with the reactions that provide them. These materials are stabilized in some manner so that they cannot easily eliminate olefin and form a second metal-oxygen bond. In the titanium example retro 2+2 would generate an allene, and in the zirconium example retro 2+2 would generate an acetylene in a small ring,

both of which are energetically unfavorable. An example of a planned synthetic strategy to an oxametallacyclobutane containing a late metal is also shown in Figure 3. Interestingly, α-oxametallcycles are known for other ring sizes. For example, there are many examples of α-oxametallacyclopentanes and α-oxametallacyclopentenes for the oxophilic metals such as titanium, zirconium and hafnium.[6] It has been postulated that the reactivity and instability of α-oxametallacyclobutanes come from the nature of the four-membered ring.[7] Four-membered rings allow extrusion of simple energetically favorable species such as olefins and acetylenes. The larger rings do not. For example, extrusion of titanium and oxygen from a α-oxatitanacyclopentane would lead to formation of a 1,3-biradical or cyclopropane, which is energetically unfavorable.

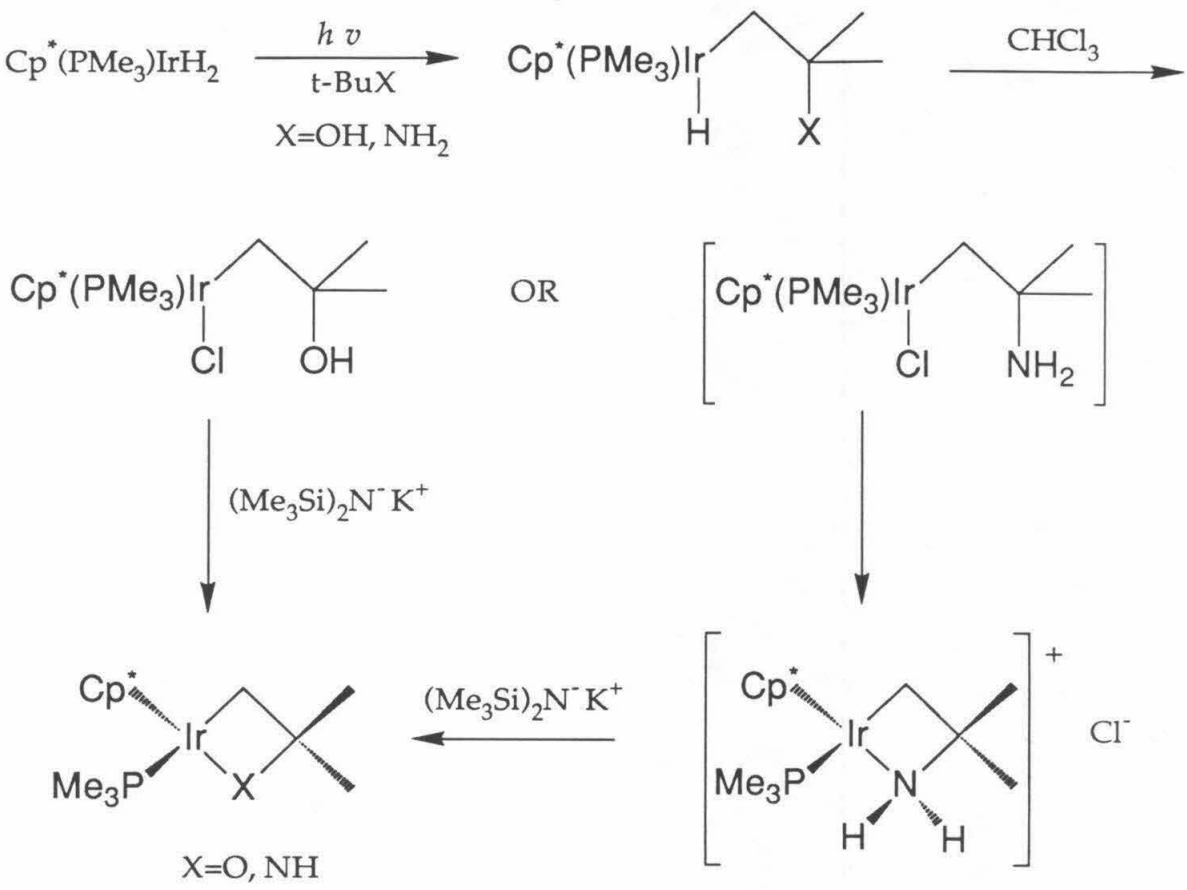


Figure 3. An example of an α-oxairidacyclobutane and an α-azairidacyclobutane.

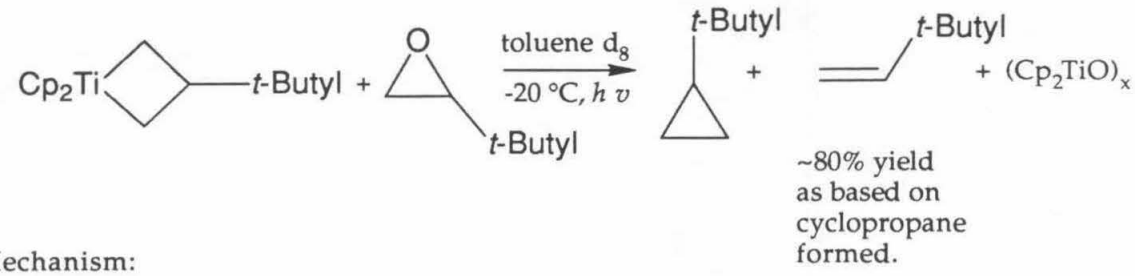
During the course of our investigation of photochemically generated titanocene with epoxides, the reaction of chemically generated titanocene with epoxides was published.[8] The titanocene used by Schobert was generated from the reaction of titanocene dichloride with one equivalent of magnesium metal in tetrahydrofuran at room temperature. The results of their investigations are qualitatively similar to ours. Schobert found that the titanocene deoxygenated the epoxide in high yield to give the olefin. Our investigations provided the same result but also indicated that the deoxygenation proceeded without any stereochemical retention. Schobert

observed strict retention of stereochemistry with trans epoxides and high retention with cis epoxides.[9] Additionally, he suggests that radicals are formed when titanocene reacts with α,β-unsaturated aldehydes. We have also found evidence for radicals. A discussion of the similarities and differences of our results and Schobert's results is found in the following section.

Results and Discussion:

The reaction of photochemically generated titanocene with epoxides proceeds cleanly to give titanocene-μ-oxo polymer and the olefin derived from epoxide deoxygenation. The unreacted epoxide remains unchanged during the reaction. The reaction of titanocene with 2.8 equivalents of neohexene oxide (1,2-epoxy-3,3-dimethylbutane) gives neohexene in a 78% yield based on the amount of cyclopropane formed. It has already been demonstrated that the reductive elimination of cyclopropane from the starting metallacycle is quantitative. The yield of this deoxygenation reaction could be improved slightly by using more equivalents of neohexene oxide. This is believed to be a result of more efficient trapping of the intermediate titanocene. Failure to trap titanocene rapidly allows the titanocene to react with itself or the solvent. No intermediates were observed in the reaction. The reaction is shown below in Figure 4.

Net Reaction:



Mechanism:

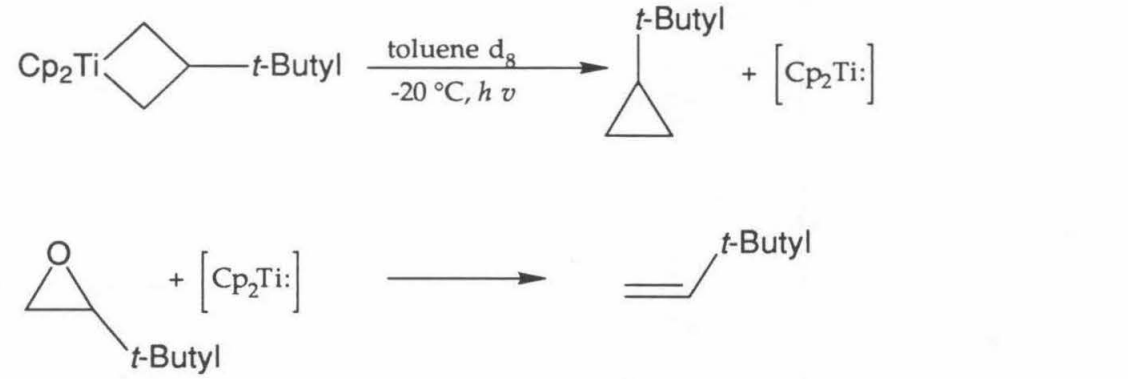


Figure 4. Epoxide deoxygenation by titanocene.

A series of different mechanisms were envisioned to account for the observed reactivity. The first mechanism was a concerted deoxygenation of the epoxide by titanocene to give the olefin and titanocene-μ-oxo. The titanocene-μ-oxo oligomerizes to an uncharacterizable material. Similar to this mechanism is the observation that titanocene (photochemically generated from the neohexene metallacycle) deoxygenates dimethylsulfoxide in an 85-95% yield[10] as shown in Figure 5.

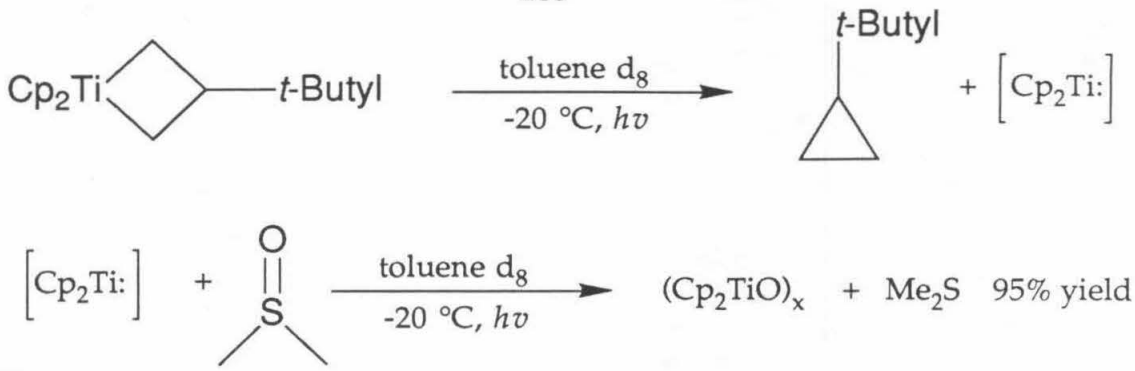


Figure 5. Dimethyl sulfoxide deoxygenation.

Alternative to this concerted reaction would be a stepwise reaction, involving a transient α-oxatitanacyclobutane, a 1,2-metallaoxetane. Metallaoxetanes are also invoked as intermediates in the Wittig chemistry that titanocene alkylidenes undergo. Low-temperature NMR studies were undertaken in order to determine if oxatitanacyclobutanes are formed transitorily in the reaction of titanocene with epoxides. No intermediates were observed in the reaction of 1,1-diphenylethylene oxide with titanocene at -65 °C. At -65 °C only 1,1-diphenylethylene was observed in a 91% yield.

Based on the thermal stability of the aliphatic metallacycles, oxametallacycles, which could be expected to be most stable with respect to 2+2 cleavage to olefin and titanocene-μ-oxo, would be the ones derived from norbornene oxide and neohexene oxide. The β-*tert*-butyltitanacyclobutane is stable to approximately 20 °C.[11] It is well known that the norbornene metallacycle is thermally stable to ~60 °C.[12] This most likely arises from the additional ring strain induced in the retro 2+2 cleavage of the metallacycle to the olefin and titanocene alkylidene. Figure 6 shows these relationships. It is important to note that this assumes that the oxametallacyclobutane has the same geometry as the metallacycle. If the oxametallacyclobutane is puckered so as to allow the lone pair on the

oxygen to donate electron density to the metal, then unfavorable steric interactions would be generated. This could mean an inherent instability for the oxametallacyclobutanes.

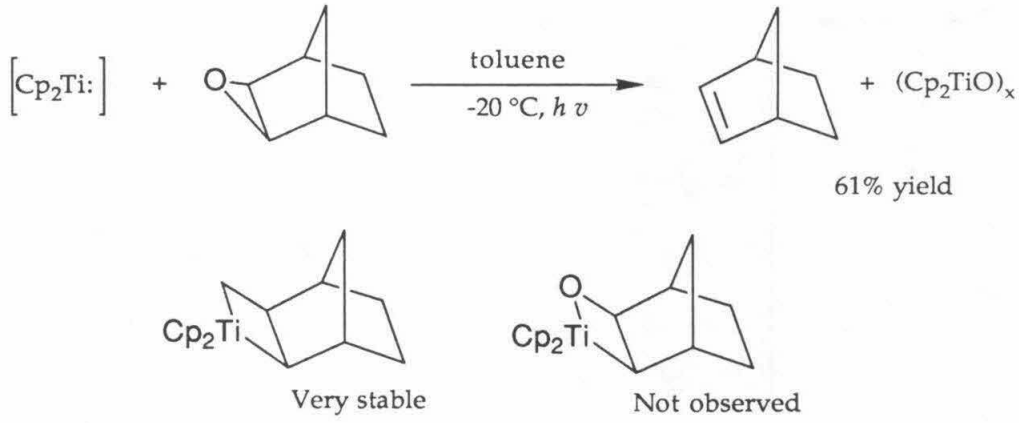


Figure 6. Titanocene and norbornene oxide reaction.

Norbornene oxide was deoxygenated in a 45-61% yield in deuterated toluene at -20 °C. No intermediates were observed during the reaction. However, extreme low temperatures were not employed. Rather than investigate other epoxides at lower temperatures, it was felt that more could be learned from labeling studies that would differentiate between a concerted reaction and a stepwise reaction. It should be noted that observation of retention does not necessarily imply a concerted reaction, but observation of scrambling does imply a stepwise reaction. Retention of stereochemistry has been observed in 1,4-biradicals generated from highly substituted cyclobutanes. Retention could result from stereospecific insertion of titanocene into an epoxide carbon-oxygen bond followed by rapid cleavage of the metallacycle. Retention could also result from generation of a 1,4-biradical provided that rotation is much slower than cleavage. The concept of the 1,4-biradical is discussed later. These different concerted types of mechanism are shown in Figure 7.

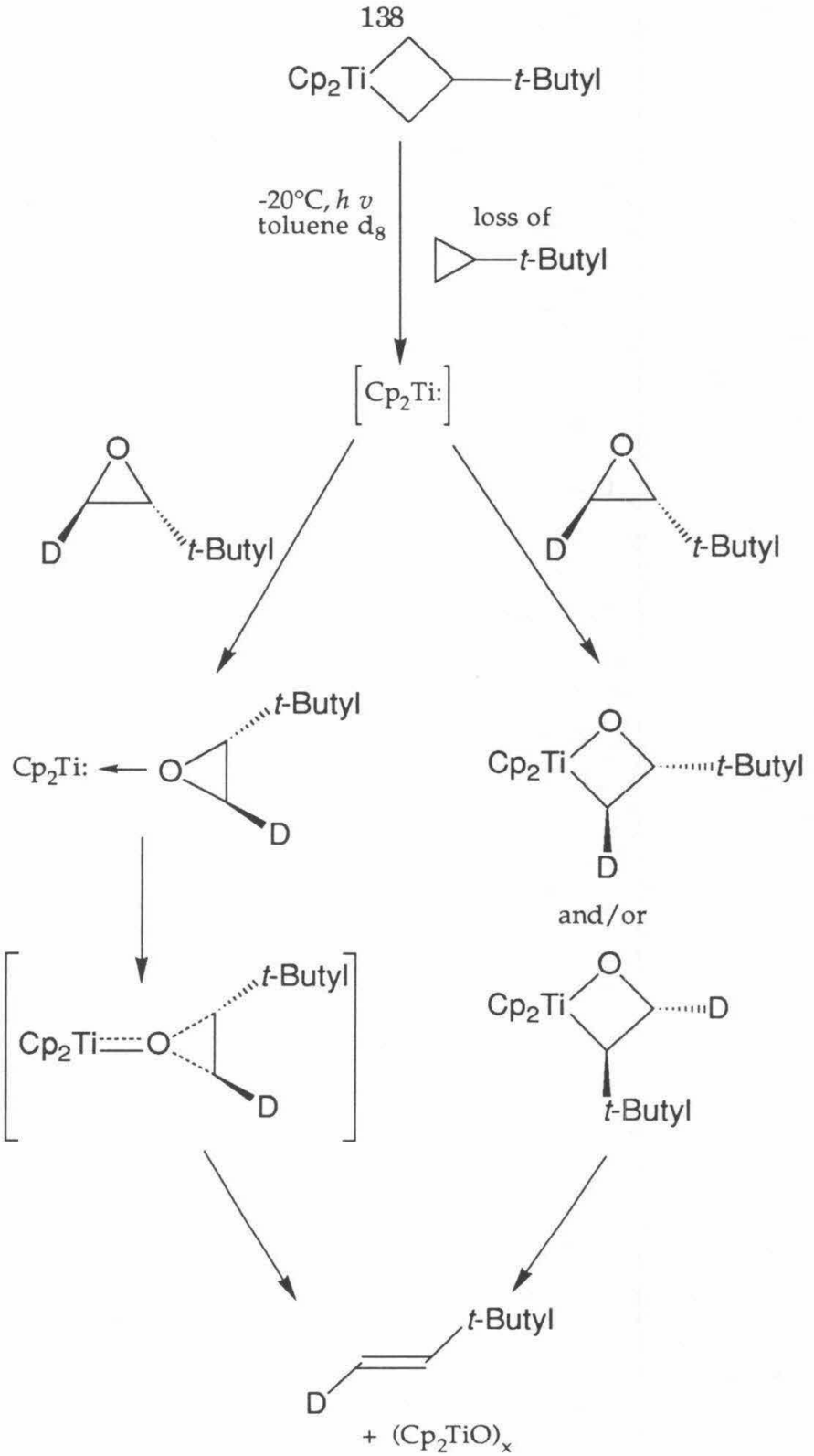


Figure 7: Possible mechanisms for stereochemistry retention.

Reaction of trans-styrene oxide-d_1 with titanocene, photochemically generated from the β-*tert*-butyltitanacyclobutane in toluene d_8 generated equal amounts of both trans deuterostyrene and cis deuterostyrene. Additionally, reaction of titanocene with trans-1-deutero-3,3-dimethyl-1,2-epoxybutane (trans deutero neohexene oxide) yielded equal amounts of both cis and trans 1-deutero-2,2-dimethyl-1-butene. The results of this reaction are shown in Figure 8. This result is somewhat different from that found in Schobert's investigations.[13] We rationalize the difference in results as stemming from the different method used to generate the titanocene and the difference in epoxides used.

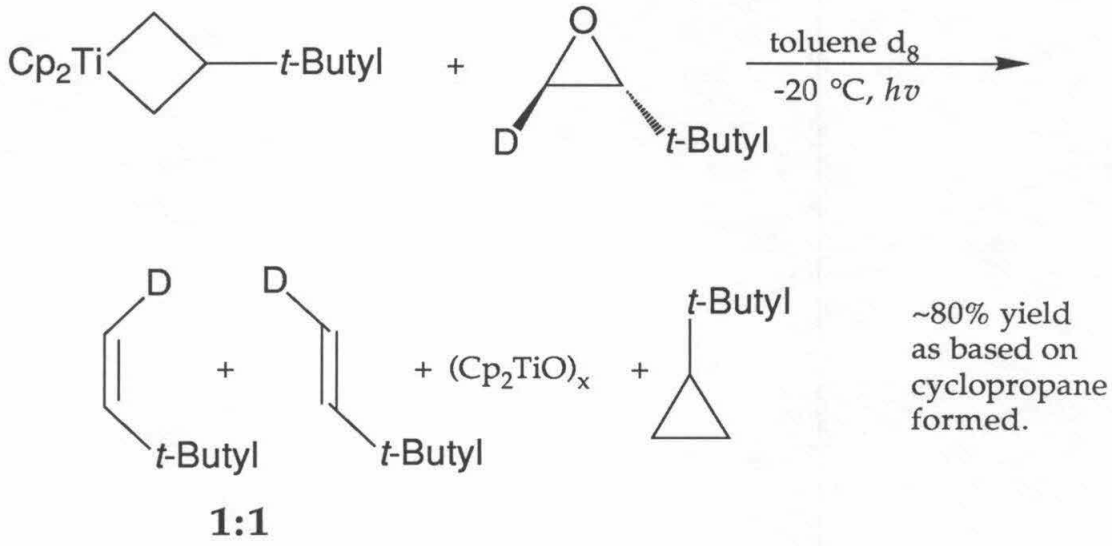


Figure 8. Stereochemical studies on epoxide deoxygenation.

In Schobert's studies, exclusive retention of stereochemistry with trans epoxides is not surprising for a number of reasons. First, trans olefins are the thermodynamically more stable in the cases examined. Second, using large groups on the epoxide as indicators of stereochemistry

is somewhat misleading in that the larger the group, the less likely it is to isomerize. In the study of organic 1,4-biradicals it was found that when large substitutes are present in stereochemically labelled materials, more retention was observed than in identical materials containing smaller groups. These large groups require more time to isomerize than smaller groups.[14] This is also evidenced by the difference in rotational barriers in substiututed and unsubstituted ethanes. This barrier to isomerization may be exacerbated by the cyclopentadienyl rings, which may slow rotation of bonds in the wedge. Third, it is not known what role the magnesium chloride formed may play in the reaction. Magnesium and magnesium chloride are oxophilic and may play a noninnocent role in the deoxygenation. The magnesium chloride may coordinate to the titanocene somehow changing its intrinsic reactivity.

A series of control experiments were undertaken to determine that the isomerization was not a result of the reaction conditions. First, at no time were any products associated with carbene generation observed. It is known that epoxides generate oxygen-substituted carbenes upon photolysis with short wavelength light. The photolysis was also pyrex-filtered to attenuate the shorter wavelengths. Second, a photolysis of a metallacycle and epoxide in toluene was carried out in the presence of excess, pure trans-1-deutero-2,2-dimethyl-1-butene. Isomerization of the added olefin was not observed during the course of the reaction. This implies that neither the products, the starting materials, nor the photolysis were responsible for the isomerized olefin produced. Third, stopping the photolysis at low conversion indicated that the stereochemistry of the resulting olefin was constant throughout the reaction, that is to say, a 50:50 mixture of isomers at all times. Fourth, it is important to note that excess

trans-1-deutero-3,3-dimethyl-1,2-epoxybutane was not isomerized during the course of the reaction. The observation that excess starting material is not isomerized during the reaction indicates that the reaction is irreversible.

The isomerized olefin produced was rationalized as resulting from a stepwise insertion of titanocene into the epoxide to give a 1,4-biradical. Similar intermediates have been invoked in the deoxygenation of organic substrates by the reagent formed from $TiCl_3/LiAlH_4$.[15] This intermedate 1,4-biradical could either generate an α-oxatitanacyclobutane through

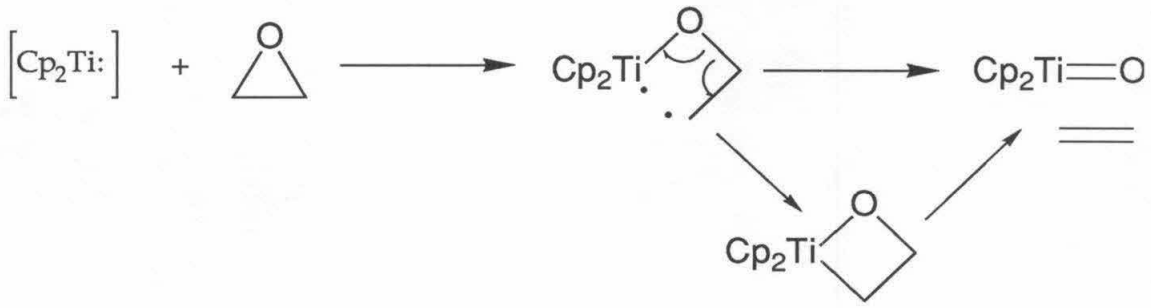


Figure 9. Closure to α-oxatitanacyclobutane may or may not occur.

closure or directly decompose to olefin and titanocene-μ-oxo. These two possibilities are shown in Figure 9. The full mechanism is illustrated in Figure 10. The 1,4-biradical is attractive for a number of reasons. First, it is the simplest way to explain the observed isomerization. Second, it is conceptually similar to the 1,4-biradical invoked in Chapter 1 to account for the isomerization of stereolabelled metallacycles. Third, a stepwise insertion into a carbon oxygen bond is what would be expected for triplet titanocene. Titanocene has been calculated to be triplet.[16] However, rationalizing the results as being due to the spin state of titanocene is not

without problems. A large spin-orbit coupling may make the spin state meaningless.

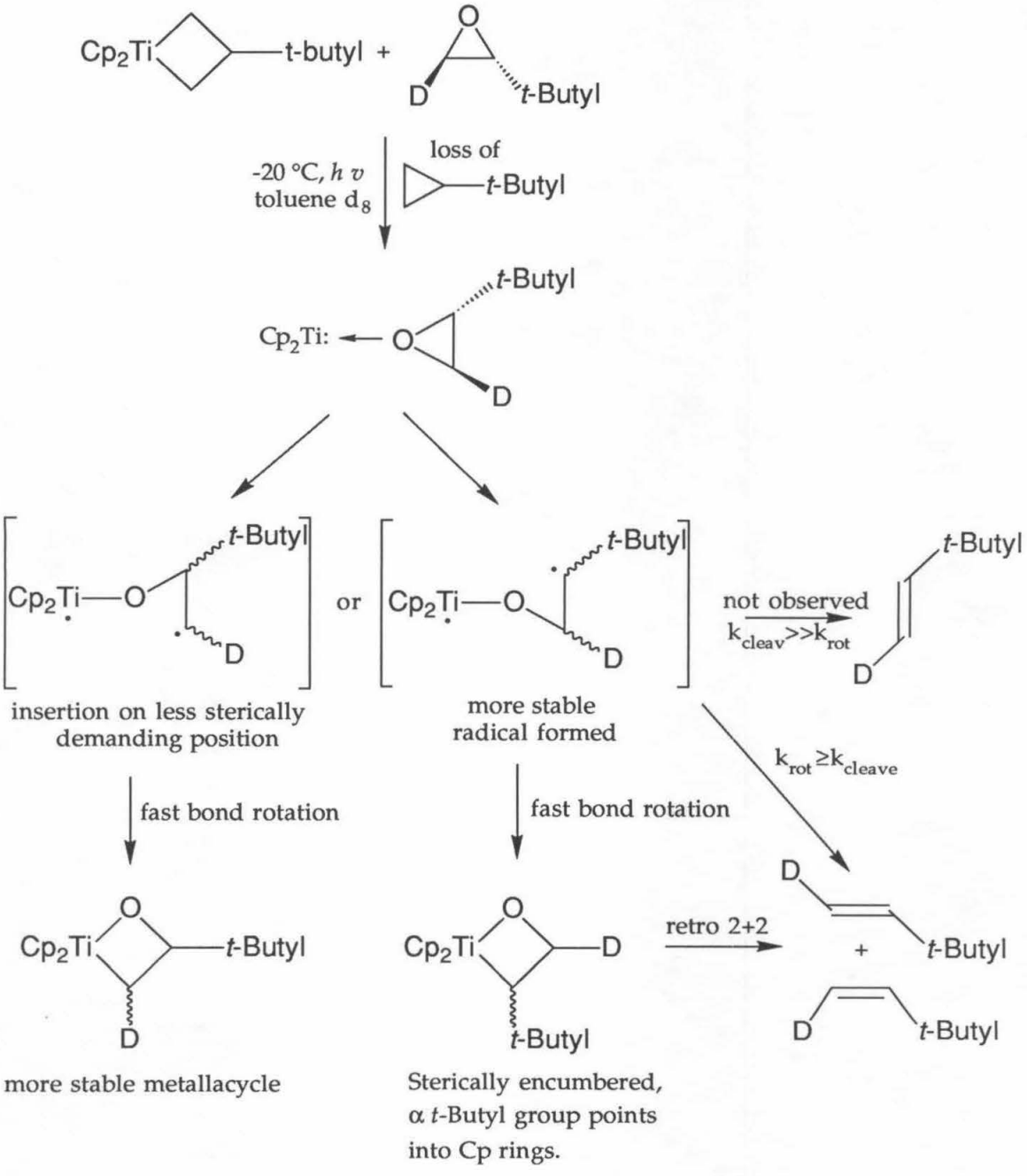


Figure 10. Explanation of observed stereochemical results.

Insertion of a titanocene into an epoxide to give an α-oxatitanacyclobutane with retention followed by photochemical isomerization can be discounted. While photochemical isomerization of stereolabelled metallacycles is documented in Chapter 1, it is unlikely in this reaction since the reaction can be carried out at a temperature (-20 °C), above which the oxatitanacyclobutane is expected to be stable. Reaction of a titanium methylidene source with pivaldehyde results in facile methylene transfer at -20 °C. The presumed intermediate of this methylene transfer reaction, an α-oxa-β-*tert*-butyltitanacyclobutane, is believed to result from 2+2 addition of the titanium methylidene and the carbonyl.[17] This is the same intermediate that would be generated from insertion of titanocene into a carbon-oxygen bond of neohexene oxide. This intermediate is not observed at low temperature in this Wittig-like reaction; hence, it is unlikely that the isomerization results from secondary photolysis of this species. Photochemical isomerization of the stereolabelled metallacycles is fairly slow under the typical photochemical conditions.

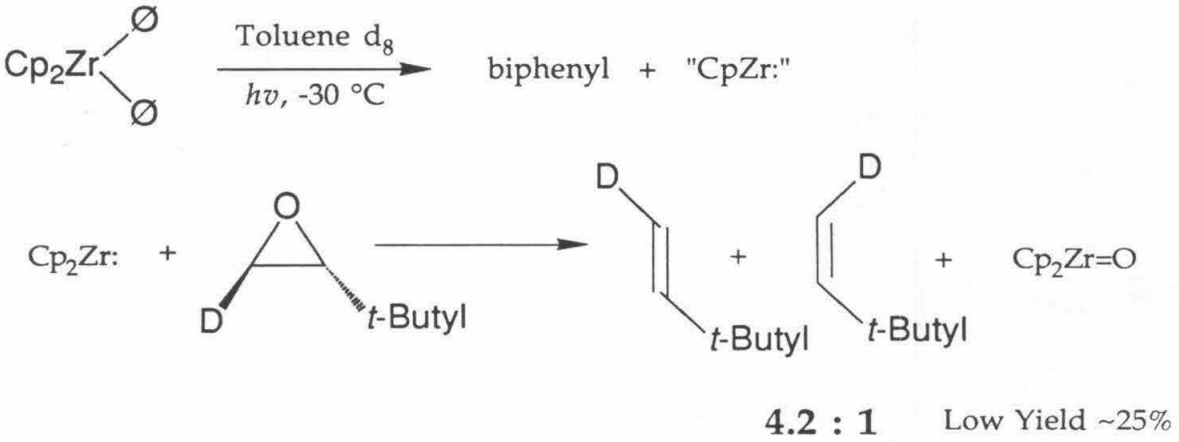


Figure 11. Stereochemistry of epoxide deoxygenation by zirconocene.

For comparative purposes the reaction of photochemically generated zirconocene[18] and labelled epoxides was investigated, and the results are shown in Figure 11. Irradiation of diphenylzirconocene in toluene d_8 at -25 °C in the presence of 3,3-dimethyl-1,2-epoxybutane gave a low yield (ca 28%) of 3,3-dimethylbutene. The reaction was not as clean as with the photochemically generated titanocene; consequently, the volatiles were used to measure the yield. Repetition of the experiment using trans-1-deutero-3,3-dimethyl-1,2-epoxybutane provided 21% yield of a 4.2 ratio of trans-1-deutero-3,3-dimethyl-1-butene and cis-1-deutero-3,3-dimethyl-1-butene. This was extremely surprising since the large difference in sizes of zirconium and oxygen would lead one to believe that the driving force to generate the π bond would be less. This presumed lesser driving force would be expected to lower the rate of cleavege relative to the rate of bond rotation in the 1,4-biradical. If the intermediate was a 1,4-biradical, then one would expect total isomerization if the intermediate were truly longer lived. However, it is possible that zirconocene and titanocene react with epoxides in two entirely different manners. In simple diatomic molecules zirconium oxygen bond is given as 181.6 kcal/mole, and titanium oxygen bond is given as 158.2±3.7 kcal/mole.[19] Perhaps the greater driving force of the reaction to generate a second zirconium oxygen bond means that the zirconium-centered 1,4-biradical cleaves even faster than the titanium centered 1,4-biradical. If this rate acceleration were enough to place the rate of cleavage on the order of a bond rotation, then retention would be the expected product. Again, this reasoning does not take into account the differences associated with sigma and pi bonds of the metal to oxygen.

The reaction of titanocene with episulfides was investigated. Titanocene reacts with propene episulfide (3 equivalents) in toluene at -20

°C to give titanocene-μ-sulfide[20] and propene in a 67% yield. This reaction is shown in Figure 12.

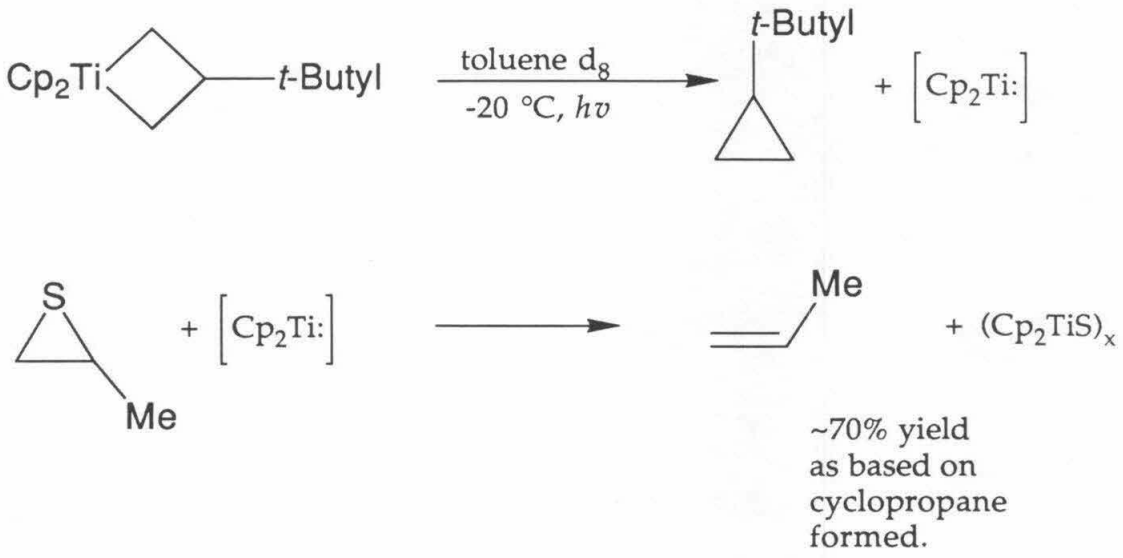


Figure 12. Reaction of titanocene and episulfides.

The stereochemistry of this reaction was investigated and is illustrated in Figure 13. Reaction of titanocene with trans-styrene episulfide d_1 in toluene at -78 °C followed by examination of the volatiles revealed that a 50:50 mixture of cis and trans styrene d_1 was generated. This result was surprising. Episulfides can be thought of as a sulfur datively bound to an olefin. This is one way of explaining why the sulfur is more weakly bonded to olefins in episulfides than is the oxygen in epoxides. The observation that the stereochemistry of the olefins resulting from stereolabelled episulfides is scrambled after desulfurization by titanocene gives added strength to the 1,4-biradical intermediate. This weaker bonding would be expected to result in retention of stereochemistry if a mechanism other than the 1,4-biradical were operating.

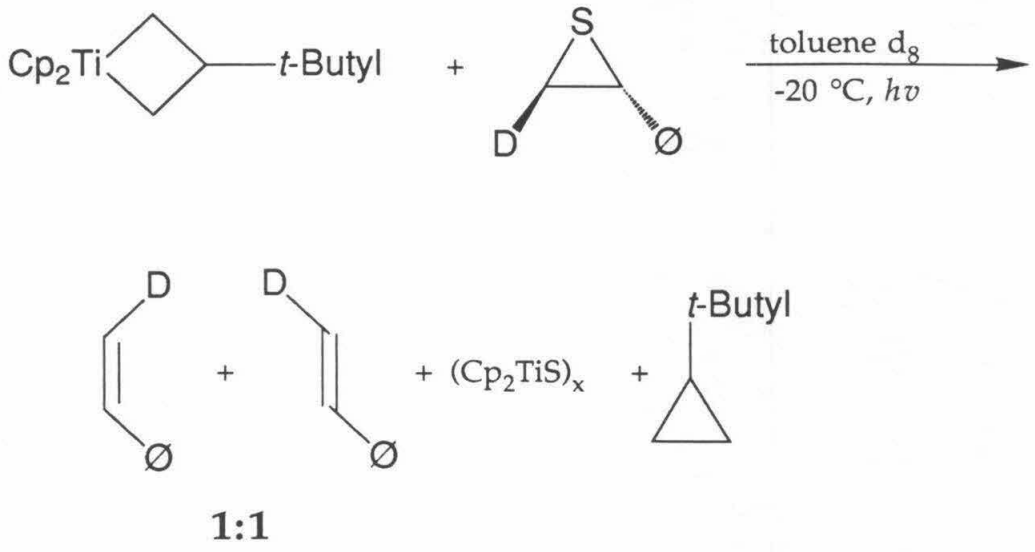


Figure 13. Stereochemistry of the reaction of titanocene and episulfides.

The reaction of titanocene with aziridenes was also investigated, Figure 14. Insertion of transition metals into aziridenes has been previously observed; α-azametallacyclobutanes were postulated as intermediates in one of the possible mechanisms of the carbonylation of aziridenes to β-lactams.[21] It was hoped that changing an oxygen in the epoxide for a nitrogen would make it possible to observe intermediates during the course of the reaction. This was not realized. Titanocene reacted with both 2-phenylaziridene and N-methyl-2-phenylaziridene to give complicated product mixtures. There are indications that the reaction of titanocene with N-methylphenylaziridene yielded a trace of a species that could be rationalized as N-methyl-α-aza-β-phenyltitanacyclobutane. The low yield of the reaction precluded isolation of the product or further characterization. In both reactions, no styrene was observed. These results were rationalized in that the N-methyl-2-phenylaziridene is

sterically more crowded than either epoxides or episulfides. The 2-phenylaziridene contains an acidic proton, which can complicate reactions with very air- and moisture-sensitive materials. The reaction of titanocene with aziridenes was not further investigated.

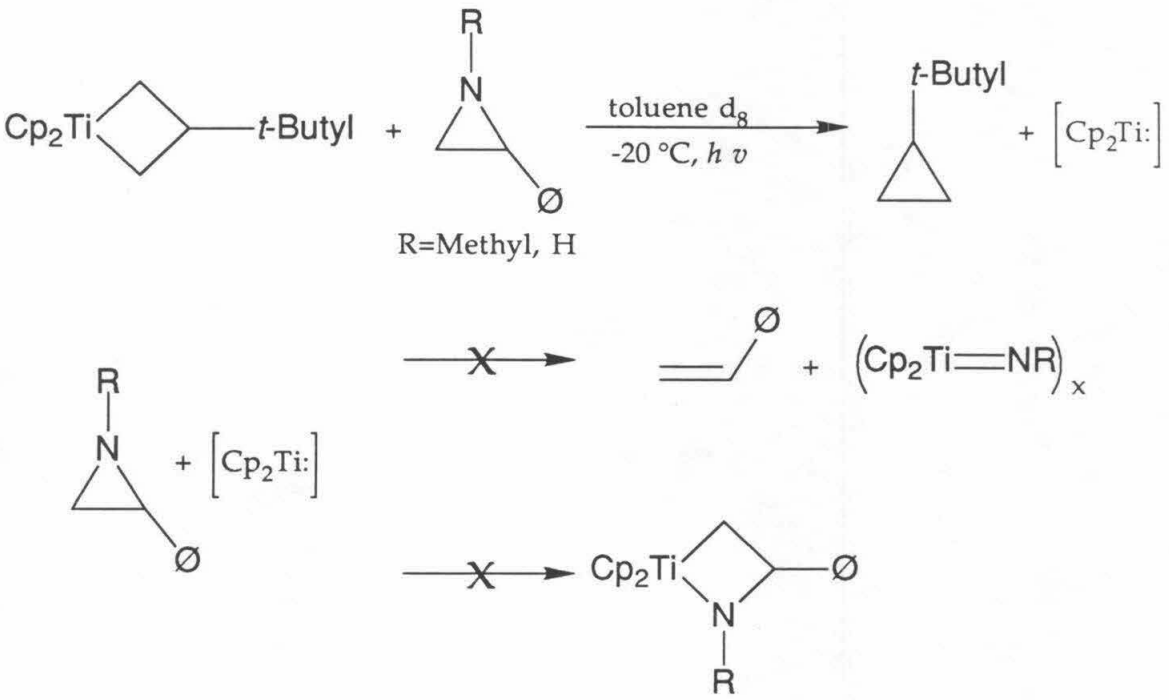
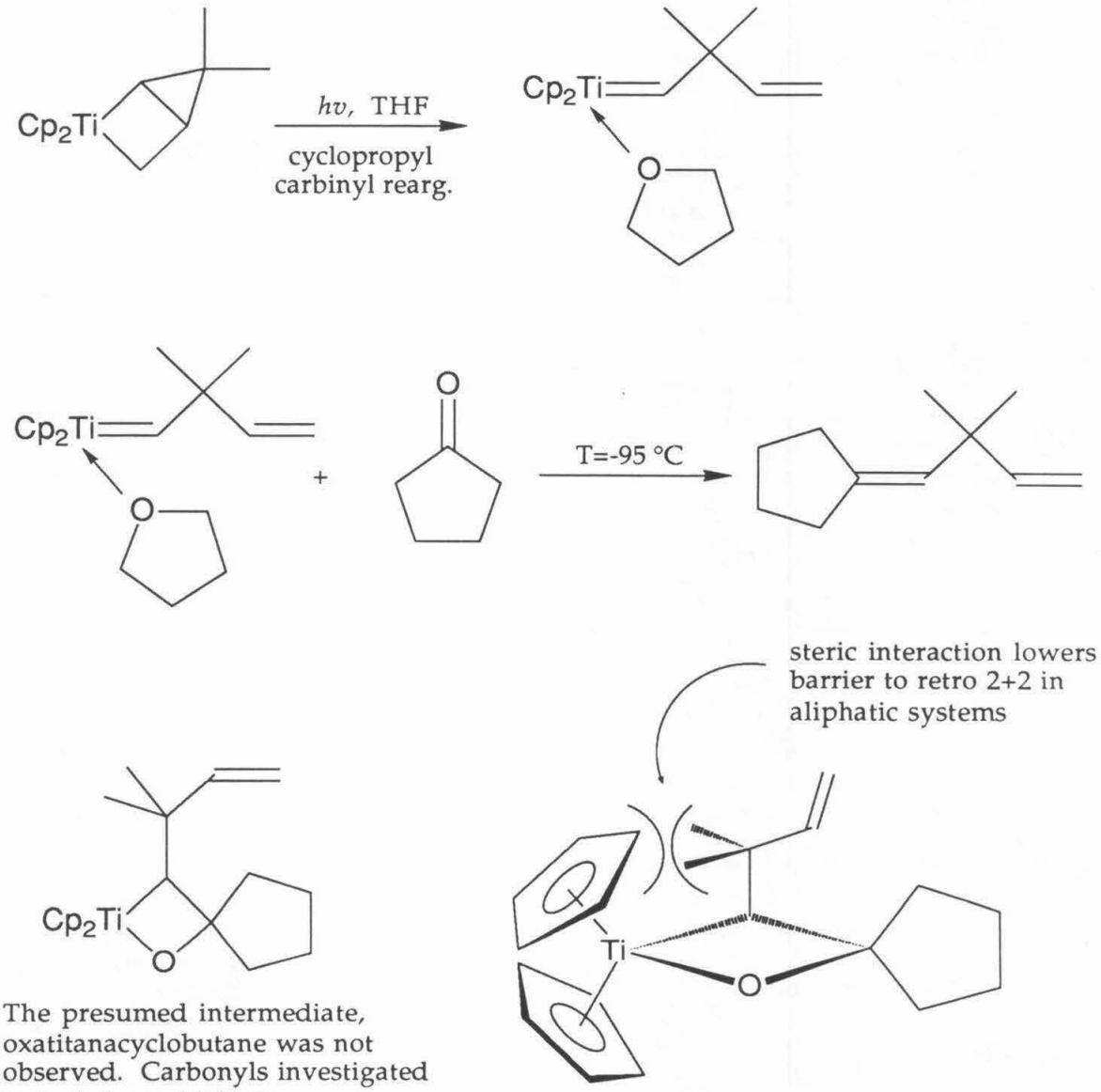


Figure 14. Aziridenes did not react with titanocene.

These collective results suggest that the metal-centered 1,4-biradical does not close to form an α-oxatitanacyclobutane. It would be thermodynamically more favorable to immediately generate an olefin and a metal oxygen double bond. Closing the ring to a cyclobutane would likely be uphill. Organic 1,4-biradicals often undergo cleavage of the center bond. The extra driving force of generating a titanium oxygen bond may preclude formation of this intermediate. While it is difficult if not impossible to prove

that the 1,4-biradical intermediate closes, it was possible to find another possible entry to the oxatitanacyclbutane reaction surface. α-Oxatitanacyclobutanes are intermediates in the Wittig-like chemistry that titanium methylidenes and titanium alkylidenes undergo.



The presumed intermediate, oxatitanacyclobutane was not observed. Carbonyls investigated include benzaldehyde, benzophenone, cyclpentanone.

Figure 15. Alkylidene transfer failed to provide evidence for an α-oxatitanacyclobutane at low temperature.

The α-oxatitanacyclobutane is generated from the 2+2 cyclo-addition of the organic carbonyl to the metal-carbon double bond. As was shown in the first chapter, it is possible to generate carbon-titanium double bonds at very low temperatures by photolysis of the metallacycle derived from dimethylcyclopropene. Reaction of this titanium alkylidene with benzophenone, benzaldehyde, and cyclopentanone at temperatures as low as -100 °C, -95 °C, and -90 °C, respectively, did not generate any species that could be identified by NMR as an oxatitanacyclobutane. The reaction is shown in Figure 15. In a typical experiment, 3 equivalents of cyclopentanone and the dimethylcyclopropene metallacycle in THF was irradiated at -95 °C. Following the photolysis, the reaction was transferred at -95 °C to an NMR spectrometer. No signals attributable to an oxatitanacyclobutane were observed. Only products associated with alkylidene transfer were observed. A control experiment (same reaction conditions without photolysis) indicated that no thermal chemistry was taking place. This was also true for the benzaldehyde and benzophenone reactions. It should be noted that these oxatitanacyclobutanes are not the same ones that would be generated from the reaction of titanocene and the epoxides studied. Additionally, these α-oxatitanacyclobutanes are expected to be extremely sterically crowded. The alpha substituents on the ring point into the cyclopentadienyl rings. This type of steric congestion makes the aliphatic metallacycles more prone to retro 2+2 cleavage and by analogy should destabilize the oxatitanacyclobutane. Attempts to labelize photochemically the trimethylphosphine ligand of the titanocene methylidene trimethylphosphine adduct to generate free titanium methylidene proceeded in very low yield. (The steric congestion in the

alpha position is a result of using a titanocene alkylidene instead of a methylidene.) The starting material appeared to decompose faster than methylene transfer to the carbonyl occurred.

An attempt was undertaken to trap the postulated 1,4-biradical. Reaction of 1,2-epoxy-6-heptene with titanocene in toluene was undertaken. If the biradical were long-lived enough, then an exo-cyclic cyclization might occur. Similar reactivity has been observed in the reaction of bis(cyclopentadienyl)titanium(III)chloride.[22] Reaction of 1,2-epoxy-6-heptene with titanocene resulted in ~90% yield of 1,6-heptadiene as shown in Figure 16. No materials resembling cyclopentane rings were observed. This observation places the rate of decomposition of the biradical somewhere between 1×10^5 sec^{-1}, the rate of 5-hexenyl trapping[23] and the rate of bond rotation, which could be around 1×10^9 sec^{-1}. Other radical clocks were not examined.

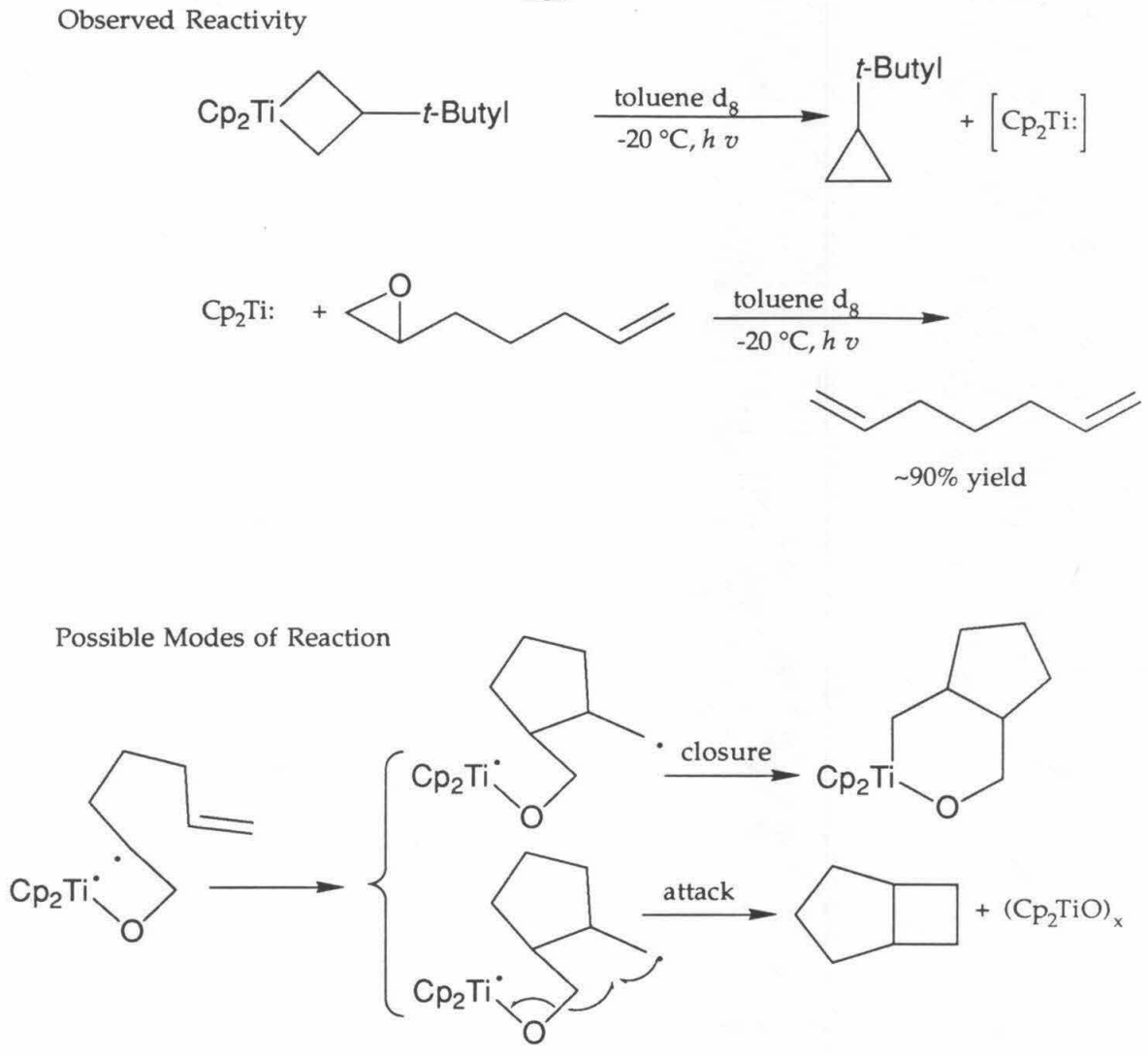


Figure 16. Attempted radical trapping.

The thermal reaction of epoxides and metallacycles was investigated. No thermal reaction occurred between an epoxide and a metallacycle at -20 °C. However, it was found that epoxides reacted with titanium methylidenes. Styrene oxide reacts with titanium methylidene (generated from a titanacyclobutane at 0 °C) to give a phenyl-substituted α–

oxatitanacyclopentane. The chemistry associated with and the mechanism of formation of this interesting and thermally stable class of compounds will be detailed in a forthcoming paper.[24] Reaction of the titanium methylidene with nonphenyl substituted epoxides resulted in intractable product mixtures from which approximately 15% olefin could be isolated. This was felt to be due to undefined reaction pathways to the thermodynamic product. Interesting the oxatitanacyclopentanes are thermally stable. The special instability of four-membered rings has been observed previously in other organometallic systems.[25]

The reaction of photochemically generated titanocene with epoxides results in formation of a β-oxa metal-centered 1,4-biradical, which undergoes cleavage to form titanocene-μ-oxo (which subsequently polymerizes), and an olefin. The reaction is believed to be stepwise based on labelling studies. Attempts to intercept the biradical failed. Interestingly, the metal-centered biradical generated from photolysis of the parent metallacycle undergoes reductive elimination to titanocene and cyclopropane, while the β-oxa metal-centered 1,4-biradical generated thermally from the reaction of titanocene and an epoxide undergoes the typical formal 2+2 cleavage reaction to yield olefin and titanocene-μ-oxo. Partial responsibility for the irreversibility of the reaction is felt to lie in the thermodynamics and the fact that the material is a 1,4-biradical and as such already well on the reaction path to product. The oxygen carbon bond may be polarized and thus may facilitate cleavage.

Experimental Section:

General Procedures. All work involving air- and/or moisture-sensitive compounds was performed using standard high-vacuum or Schlenk-line techniques under argon purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Work involving manipulation of air-sensitive compounds was accomplished under nitrogen in a Vacuum Atmospheres drybox equipped with a -40 °C refrigerator and a dry-cool recirculator. Proton, deuterium, and carbon NMR spectra were recorded on a JEOL FX-90Q (89.9 MHz ^{1}H, 22.5 MHz, ^{13}C), or a JEOL GX-400 (399.65 MHz ^{1}H, 61.35 MHz ^{2}H, 100.67 MHz ^{13}C). Proton chemical shifts are referenced to internal residual monoprotiosolvents. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Deuterium chemical shifts are referenced to natural abundance deuterium in the solvent. Gas chromatography analyses (VPC) were performed on a Shimadzu GC-Mini 2 flame ionization instrument with a 50 meter capillary column and equipped with a Hewlett-Packard model 339A integrator. Preparative VPC was performed on a Varian 920 Aerograph with a thermal conductivity detector equipped with a Hewlett Packard 7127A strip recorder (columns: 6 ft by 1/4 in., SE-30 or a 4 ft by 1/2 in. silver nitrate column for volatile olefins). Thin-layer chromatography (TLC) was performed on precoated TLC plates (silica gel 60 F-254, EM Reagents). Flash chromatography was by the method of Still et al.[26], using silica gel 60 (230-400 mesh ATMk, EM Reagents). Elemental analysis was performed at the analytical facilities of the California Institute of Technology or at Galbraith Labs. Photolyses were performed with a 450 watt high pressure mercury Hanovia lamp.

Temperatures were maintained with clear pyrex dewars filled with isopropanol at the desired temperature. Temperatures cited reflect the final temperature that the bath obtained at the end of photolysis; typically, a change of only 10 °C was observed. All photolyses were pyrex filtered unless otherwise stated.

Materials. The solvents were purified as follows: toluene, benzene, tetrahydrofuran, and diethyl ether were vacuum-transferred from sodium benzophenone ketyl into solvent flasks equipped with Teflon screw-type valves. Methylene chloride, acetonitrile, chloroform, pyridine were distilled from calcium hydride at atmospheric pressure and subsequently freeze-pump-thaw degassed. Dimethylsulfoxide was distilled from calcium hydride at reduced pressure. Solvents used in photochemical reactions (typically, THF, benzene, and toluene) were vacuum-distilled directly into the reaction vessels from thoroughly degassed solvent pots containing a small amount of sodium-potassium alloy. Metallacycles derived from Neohexene[27], and 2,2-dimethylcyclopropene[28] were synthesized from adaptations of the literature procedure. *m*-Chloroperbenzoic acid was recrystallized from methylene chloride. Benzaldehyde, cyclopentanone, 2,2-dimethyl-1-butyne (neohexyne), 1,2-epoxy-3,3-dimethylbutane (neohexene oxide), 1,6-heptadiene, propene episulfide, phenyl acetylene, styrene oxide, trimethylene oxide (oxetane), and were purchased and distilled prior to use and degassed. Benzophenone, and 2,3-epoxynorbornane (norbornene oxide) were sublimed under vacuum. Literature procedures were employed to synthesize 1,1-diphenylethylene oxide from benzophenone, trimethylsulfoxonium chloride and sodium hydride in dimethylsulfoxide and the product was carefully recrystallized prior to use.[29] N-methyl-2-phenylaziridene was synthesized from the

literature procedure[30] and was received as a gift from Joon Won Park. 2-phenylaziridene was received as a gift from Joon Won Park. It was synthesized from the reaction of sodium azide with styrene oxide.[31] The resulting 2-hydroxy-1-phenyl-1-ethylazide was treated with triphenylphosphine in diethyl ether at ambient temperature for 48 hours to give the phenylaziridene, which was distilled prior to use. Trans-styrene episulfide-d_1 was prepared jointly with Joon Won Park. The experimental given here is reproduced from his thesis.[32] Diphenyl zirconocene was prepared from phenyl lithium and zirconocene dichloride by the literature method.[33]

Trans-styrene-d_1: A 500 mL Schlenk flask was charged with 29.88 g of zirconocene dichloride (102.22 mmole) and dissolved in 350 mLs of dry THF. In 20 mLs of THF 0.9957 g of lithium aluminum hydride (26.23 mmole) was dissolved. This was cannulated into the zirconocene dichloride solution. The resulting white solid was washed three times with 10 mLs of THF and then dried under vacuum. The solid was suspended in 250 mLs of toluene and 9.50 mLs of phenylacetylene (8.83 g, 86.5 mmole). The reaction mixture was stirred 16 hours. The volatiles were removed under under vacuum. The resulting solids were washed with pentane and then suspended in diethyl ether. To this was syringed 15 mLs of D_2O (16.5 g, 0.82 moles). The reaction mixture was stirred 6 hours and then filtered. The ether was removed by distillation at ambient. The labeled styrene was distilled from a trace of BHT at 40 °C and 15 Torr to give 6.5 g (61 mmole, 72%) of product that contained a 12% proton impurity at the trans position. This resulted from inadvertent hydrolysis, not from isomerization of the product.

Trans-styrene oxide-d1: A small Schlenk was charged with 3.13 g of the trans-styene-d1 (29.8 mmole) and 50 mLs of methylene chloride. To this was added 5.20 g of *m*-chloroperbenzoic acid (30.1 mmole). The solution was stirred 24 hours, filtered and extracted with cold 10% NaOH. The mixture was dried over sodium sulphate and then was distilled to give 1.79 g (14.8 mmole, 50%) of product. ^{1}HNMR ($CDCl_3$) δ 7.32 (s, 5H, ph); 3.86 (d, 1H, J_{HH}=2.69 Hz); 2.79 (d, 1H, J_{HH}=2.69 Hz).

Trans-styrene episulfide-d1: Trifluoroacetic acid (0.64 mL, 8.3 mmol) was added to a mixture of trans-styrene oxide-d1 (1.00 g, 8.25 mmole) and triphenylphosphine sulfide (2.45 g, 8.32 mmole) in dry benzene (35 mLs) at room temperature. The solution was stirred overnight with excess sodium bicarbonate, after the solution was allowed to react for 2.5 hrs. After filtration, the solvent was removed under vacuum. Triphenylphosphine oxide was removed by filtration after the addition of 5 mLs of benzene. The product was purified by column chromatography, using benzene. ^{1}HNMR (C_6D_6) δ 7.02 (m, 5H, Ph); 3.42 (d, 1H, J_{HH}= 5.4 Hz, α–CH); 2.28 (m, 0.14, H, β-CH); 2.16 (d, 1H, J_{HH}=5.4 Hz, β-CH). The 14% trans-α-protio impurity remained. In order to prevent polymerization, the product was stored as a frozen solution in benzene at -50 °C.

Trans-1-deutero-3,3-dimethyl-1-butene: A Schlenk was charged in a drybox with 10.61 g of zirconocene hydrio chloride (41.1 mmole), prepared as described above from zirconocene dichloride and lithium aluminum hydride. The hydride was suspended in 150 mLs of toluene. To this suspension was cannulated 5.0 mLs of 3,3-dimethyl-1-butyne (3.33 g, 40.5 mmoles) dissolved in 10 mLs of toluene. The resulting solution was stirred overnight and then volatiles were removed under vacuum. The resulting solid was washed with 100 mLs of pentane. This was followed by drying

under vacuum. The solid was redissolved in 30 mLs of toluene. To this was syringed an excess of D_2O. The resulting suspension was stirred 8 hours. The volatiles were vacuum-transferred to a round-bottomed flask. The product was isolated by distillation from the toluene to give 2.60 g, 30.5 mmole, 74%. The product was isotopically pure by NMR. ^{1}HNMR (C_6D_6) δ 5.82 (dd, 1H, J_{HH}=17.5 Hz, J_{HD}=1.6 Hz, H gem to *tert*-butyl); 4.92 (d, 1H, J_{HH}=17.5 Hz, H cis to *tert*-butyl and gem to deuterium); 0.96 (s, 9H, *tert*-butyl).

Trans-1-deutero-3,3-dimethyl-1,2-epoxybutane: A small Schlenk was charged with 2.00 g of *m*-chloroperbenzoic acid (11.59 mmole) and 70 mLs of methylene chloride under argon. The solution was cooled to 0 °C, and 7.63 g of trans-1-deutero-3,3-dimethyl-1-butene (7.63 mmole) was added by cold syringe. The suspension was stirred at 0 °C for 2 hours and at room temperature for 5 hours. The volatiles were vacuum-transferred into a small round-bottomed flask. The product was isolated by distillation and subsequent preparative vapor-phase chromatography on an SE-30 column isothermally at 100 °C. The yield of the reaction was not determined, as the entire crude product was not purified by VPC. ^{1}HNMR (C_7D_8) δ 2.42 (d, 1H, J_{HH}=2.68 Hz); 2.21 (d, 1H, J_{HH}=2.68 Hz); 0.78 (s, 9H, *tert*-butyl).

1,2-Epoxy-6-heptene: A small Schlenk was charged with 0.86 g of 1,6-heptadiene (8.9 mmole, 2.9 eq) and 5 mLs of methylene chloride. A solution of 0.54 g of *m*-chloroperbenzoic acid in 10 mLs of methylene chloride wascannulated slowly into the diene at ambient temperature. The solution was stirred at room temperature for approximately 8 hours. The reaction mixture was cooled to 0 °C and filtered. The volatiles were removed under vacuum. The product was purified by preparative vapor phase chromatography on an SE-30 column isothermally at 150 °C. ^{1}HNMR

(CDCl3) δ 5.75 (m, 1H); 5.00 (d, 1H); 4.94 (d, 1H); 2.90 (br m, 1H); 2.73 (pseudo t, 1H); 2.45 (m, 1H); 2.09 (br m, 2H); 1.53 (br m, 4H).

NMR tube reaction: In a drybox, the metallacycle (typically this was the β-*tert*-butyltitanacyclobutane, since it was thermally stable and had a simple NMR spectra) was weighed into a tared NMR tube. To this was added approximately 450 μL of the deuterated solvent (typically toluene or THF). To this was then added, by microLiter syringe, the desired epoxide or episulfide. The tube was then quickly stoppered with a rubber septum, removed from the drybox, shaken to mix, and then cooled to the desired temperature (typically -20 °C). NMR spectra were recorded prior to photolysis to ensure that no thermal chemistry was occurring. NMR spectra were recorded at low temperature during the course of the photolysis by stopping the photolysis and recording the NMR spectra. Afterwards, the photolysis was restarted. Internal standards were used to determine mass loss; typically, there was negligible mass lost during the reaction. The yield of the reaction was determined by measuring the ratio of the integrated cyclopropane resonances to the resonances of the product (olefin). The ratio of starting metallacycle to epoxide was usually about 4:1. The organometallic product of the reaction of titanocene with an epoxide is titanocene-μ-oxo. This material occasionally precipitated from solution. When this occurred, it was removed by centrifuging it to the top of the NMR tube. If it appeared that the polymeric titanocene-μ-oxo was interfering with the integration of the product olefin and the cyclopropane, then the volatiles were analyzed by NMR separately. In the deuterium-labeling experiments the volatiles were also vacuum-transferred to a separate NMR tube and reexamined by NMR and capillary gas chromatography, if necessary.

Sealed NMR Tube Reaction: A sealable NMR tube was charged in a drybox with the metallacycle. On a vacuum line the solvent was condensed in, followed by the epoxide (quantitatively vacuum-transferred from a previously tared Kontes flask). The tube was sealed. Its NMR spectrum was recorded at low temperature. The tube was irradiated and reexamined. Again, the volatiles were removed and examined by NMR and vapor-phase chromatography if necessary.

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α-oxatitanacyclopentanes may be synthesized from the reaction of epoxides and titanocene methylidenes. Park, J. W.; Wysong, E. B.; Wheeler, D. R.; Grubbs, R. H. Manuscript in preparation.

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CHAPTER 4

Oxidation Chemistry of Bis(η^5-cyclopentadienyl)titanacyclobutanes

Introduction:

During investigations aimed at methylenating the carbonyl functionality of 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one, the reaction of 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one and bis(η^5-cyclopentadienyl)titanacyclobutanes was investigated. Titanacyclobutanes undergo a thermally allowed retro 2+2 cleavage to generate an olefin and an equivalent of titanium methylidene, which is a powerful methylenating agent. The result of the reaction was not the fulvene expected but rather a cyclopropane and a new organometallic product, Figure 1. This result was rationalized as a result of oxidatively induced fragmentation of the metallacycle. It is well known that 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one is a strong oxidant. This oxidatively induced fragmentation was surprising, since it is typically thought that d^0 organometallic compounds are difficult to oxidize.

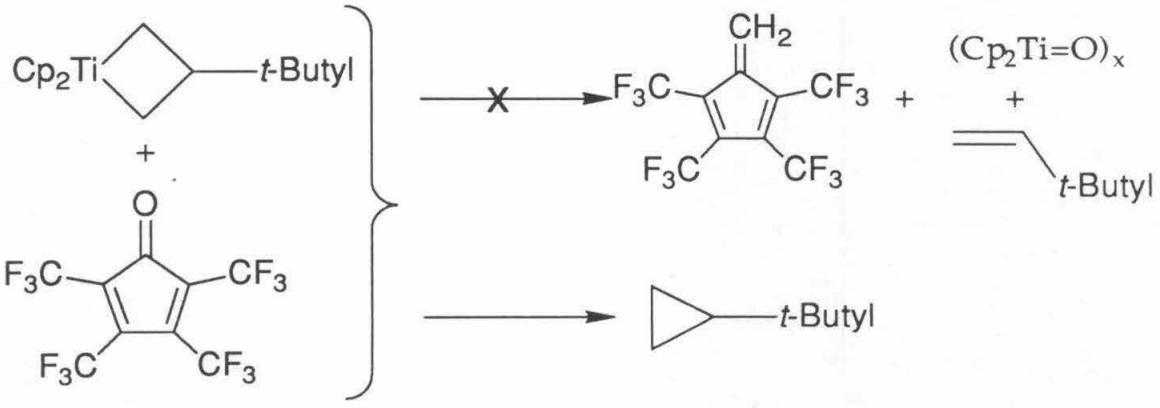


Figure 1. Oxidative elimination of cyclopropane by 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one.

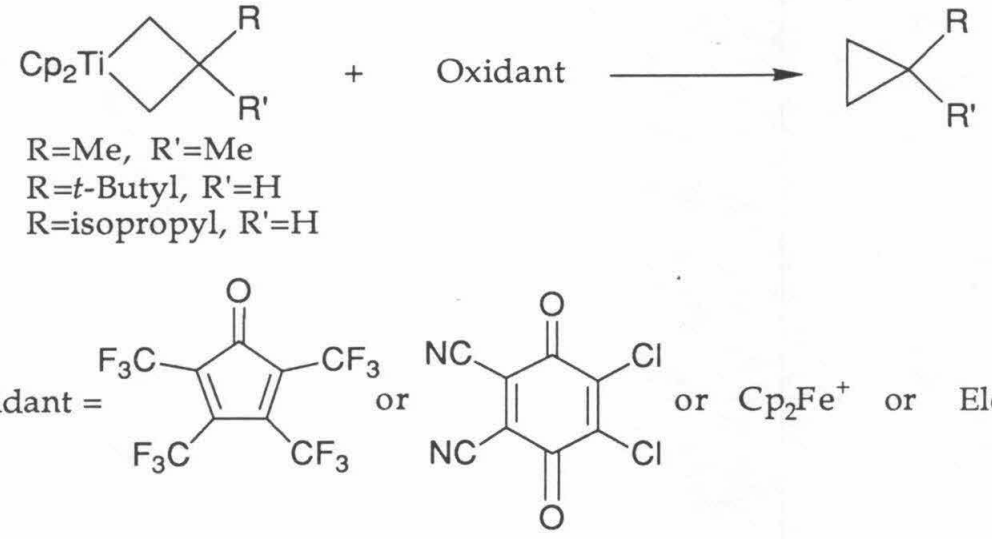
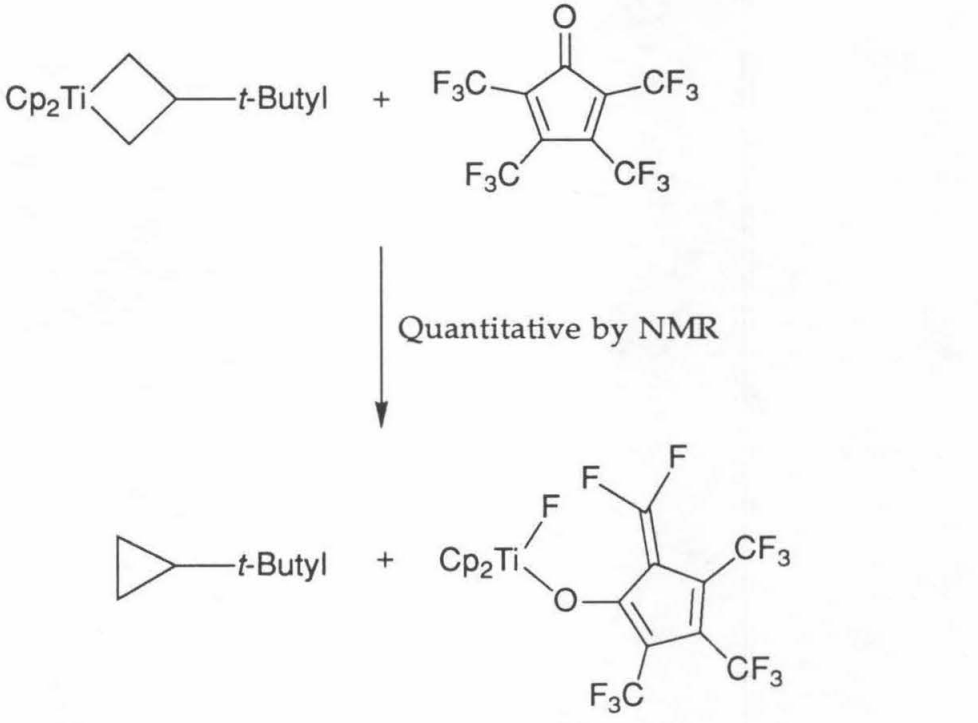


Figure 2. General oxidation of titanacyclobutanes.

In order to investigate this reaction efficiently, a collaborative investigation was undertaken involving Caltech together with Mark Burk and William Tumas of Dupont. The introduction will detail much of their initial electrochemical results, while the results and discussion section will examine the stereochemical labelling studies performed here at Caltech. It should be remembered that this work is still in progress and that much of the work is still relatively preliminary. Despite this, the synergism between photochemistry and electrochemistry has unified and deepened current understanding of the mechanism of cyclopropane formation from titanacyclobutanes. The relationship between electrochemistry and photochemistry is based on the fact that both techniques probe the electronic nature of the material being investigated.

The oxidation of a series of titanacyclobutanes[1] by 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one was investigated,

Figure 2. The reaction was found to be quantitative by ^1H NMR. The organometallic product of the reaction was identified by single crystal x-ray diffraction as the titanium enolate of the dienone shown in Figure 3. The NMR spectra were too ambiguous to allow identification of the product without x-ray crystallography. The oxidation reaction of titanacyclobutanes to give cyclopropanes was found to proceed equally well with ferrocenium ions or DDQ. However, with ferrocenium ions or DDQ, the organometallic product was not a discrete or easily characterizable material.



NMR Data (CD_2Cl_2)
^1H: δ 6.4 (Cp)
^{13}C: δ 171.1 (C-O)
^{19}F: δ -56.5, -54.7, -53.3 (mult., CF_3)
-51.5 (dd, α-CF_2), -47.5 (mult., α-CF_2)
60 (Ti-F)

Figure 3. Identification of organometallic products of the 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one oxidation.

While expanding the scope of the chemistry to include zirconocene, it was found that diphenylzirconocene yields biphenyl upon oxidation with either 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one or DDQ. This result is similar to some of the oxidation results that have been observed by Jordan and coworkers. They found that dimethylzirconocene upon oxidation by silver tetraphenylborate yields an unquantified amount of ethane in addition to a zirconocene methyl cation.[2] In a similar reaction, Jordan found that oxidation of dibenzylzirconocene with ferrocenium tetraphenylborate in tetrahydrofuran yielded half an equivalent of 1,2-diphenylethane, the benzyl coupling product. This is shown in Figure 4. The organometallic product was the THF adduct of zirconocenebenzyl cation.[3] In these studies, a complete reaction was not proposed, but it was thought to involve radicals, since traces of benzylferrocene were observed in the ferrocenium oxidation of dibenzylzirconocene. Jordan's work is believed by the author to be the only other study of d^0 metallocene oxidation.

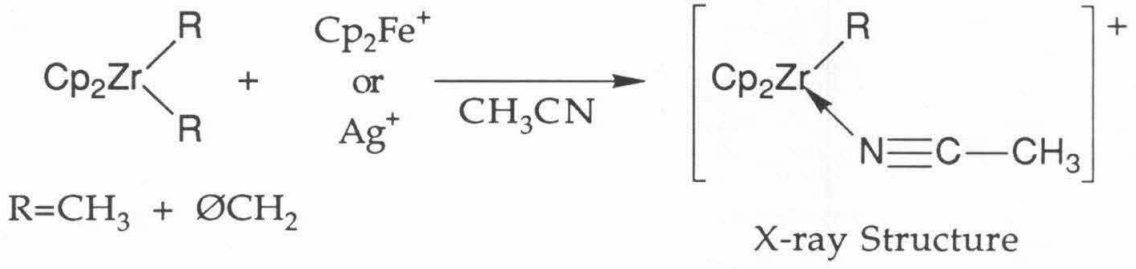


Figure 4. Other oxidations of early d^0 transition metal complexes.

The oxidation of β-*tert*-butyltitanacyclobutane was studied, using electrochemical means. In acetonitrile with 0.1 M tetrabutylammonium tetraphenylborate as the electrolyte, the oxidation potential of the

titanacyclobutane was found to be 0.64 V vs. SCE and 0.33 V vs. Ag/Ag^+ ($AgNO_3$). The oxidation was not reversible. Bulk electrolysis allowed the organic products to be identified. The organic product was *tert*-butylcyclopropane, the same product as found in the chemical oxidations. The heterogeneous electron transfer rate was measured by a rotating disk electrode as $3x10^{-4}$ cm sec^{-1}.

The intermolecular electron transfer rate constant between β-*tert*-butyltitanacyclobutane and ferrocenium was measured by the method of Saveant and Vianello.[4] The technique was applied to ferrocene, methylferrocene and 1,1'-dimethylferrocene. A plot of the logarithm of the rate of electron transfer as a function of driving force, $E_0(Ti)$-$E_0(Fe^+)$, yields a straight line as predicted by Marcus theory. Figures 5, 6, and 7 show some sample cyclic voltammograms and the resulting plots of rate vs. potential.

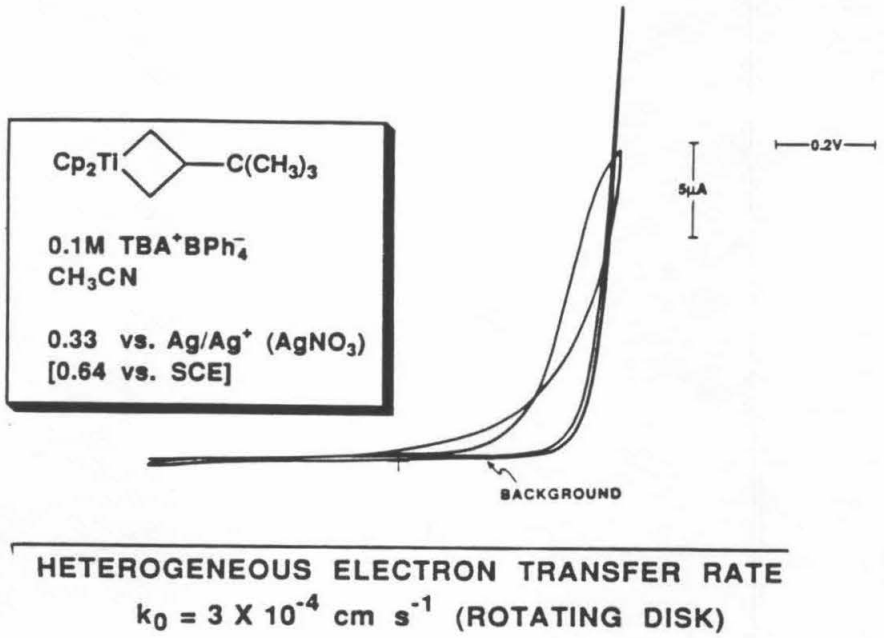


Figure 5. Cyclic voltammogram of titanacyclobutane oxidation.

Figure 6. Mechanism of kinetic data.

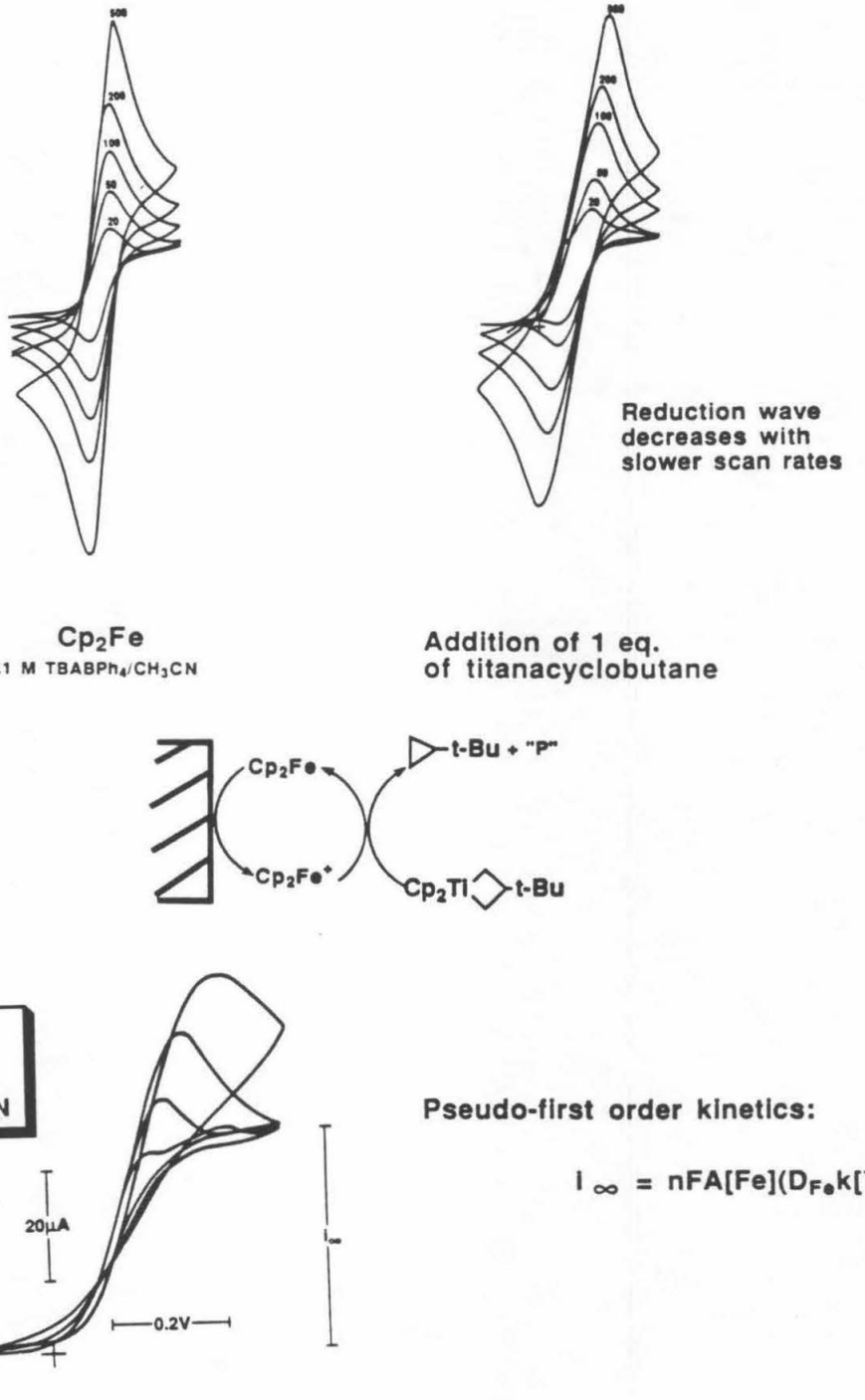
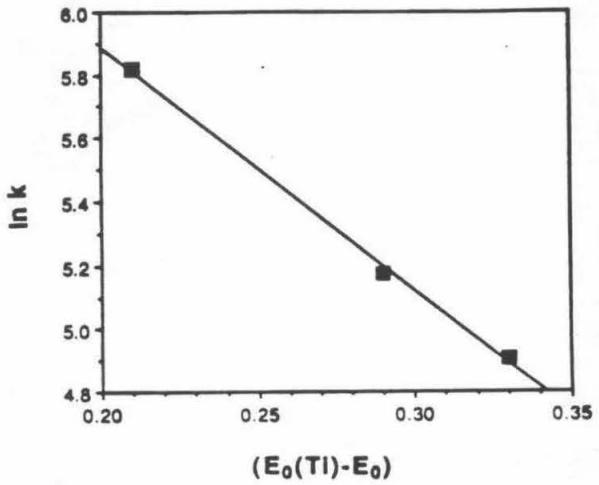


Figure 7. Linear correlation between rate of electron transfer and redox potential.

Ferrocene	*E_0(V vs. SCE)*	*k ($M^{-1}s^{-1}$)*
ferrocene $[Cp_2Fe]$	0.41	340
1-methylferrocene [(CpMe)CpFe]	0.33	180
1,1'-dimethylferrocene $[(CpMe)_2Fe]$	0.29	140



Linear correlation between reaction rate and redox potential of metallocene (Marcus Equation)

Current work includes attempts to perform ESR studies on the transiently formed radical cation by performing the oxidation in the probe of an ESR spectrometer. Additionally, the oxidation is being examined with other oxidants, d^0 metal compounds, and d^0 bimetallic systems. The successful oxidation of d^0 organometallic species by both Jordan and our group potentially provides the opportunity to generate interesting materials previously thought to be inaccessible or difficult to synthesize. Furthermore, information gained from electrochemistry about titanacyclobutanes could help verify the observations and hypotheses concerning the photochemical reductive elimination of cyclopropanes discussed in the first chapter. Photochemistry and electrochemistry are both means to investigate the electronic nature of materials and therefore can provide complementary information by different routes. With the goal of greater understanding and potential for corroborating the theories put forth in Chapter 1, the mechanism of the oxidatively induced fragmentation was investigated.

Results and Discussion:

The chemical oxidation of a series of metallacycles was investigated. In order to learn more about the mechanism of the reductive elimination, the oxidation was investigated using stereolabelled metallacycles. As was explained in Chapter 1, if the cyclopropane is formed with 100% retention of stereochemistry relative to the metallacycle, then a concerted reaction is indicated. If the cyclopropane is generated with less retention, then a stepwise reaction is more likely. These mechanisms are illustrated in Figure 8.

Because the oxidants were relatively insoluble and became paramagnetic after oxidation, NMR could be employed only to examine the volatile products of the reaction. An exception to this was 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one which, after oxidation of the organometallic species, went on to generate diamagnetic species.

Reaction of stereolabelled metallacycles **1** and **2** with dichlorodicyanoquinone (DDQ) in methylene chloride resulted in formation of cyclopropanes. Integration of NMR resonances (^{1}H NMR for **1** and ^{2}DNMR for **2**) indicated a 5.5±1 to 1 retention/isomerization, Figure 9. This ratio was very similar to that found in the early stages of the photochemically induced reductive elimination. Control experiments clearly indicated that the cyclopropane was not isomerized by excess DDQ. Reaction of a pure sample of trans-2-deutero-isopropylcyclopropane in methylene chloride with excess DDQ showed no change after 24 hours at room temperature.

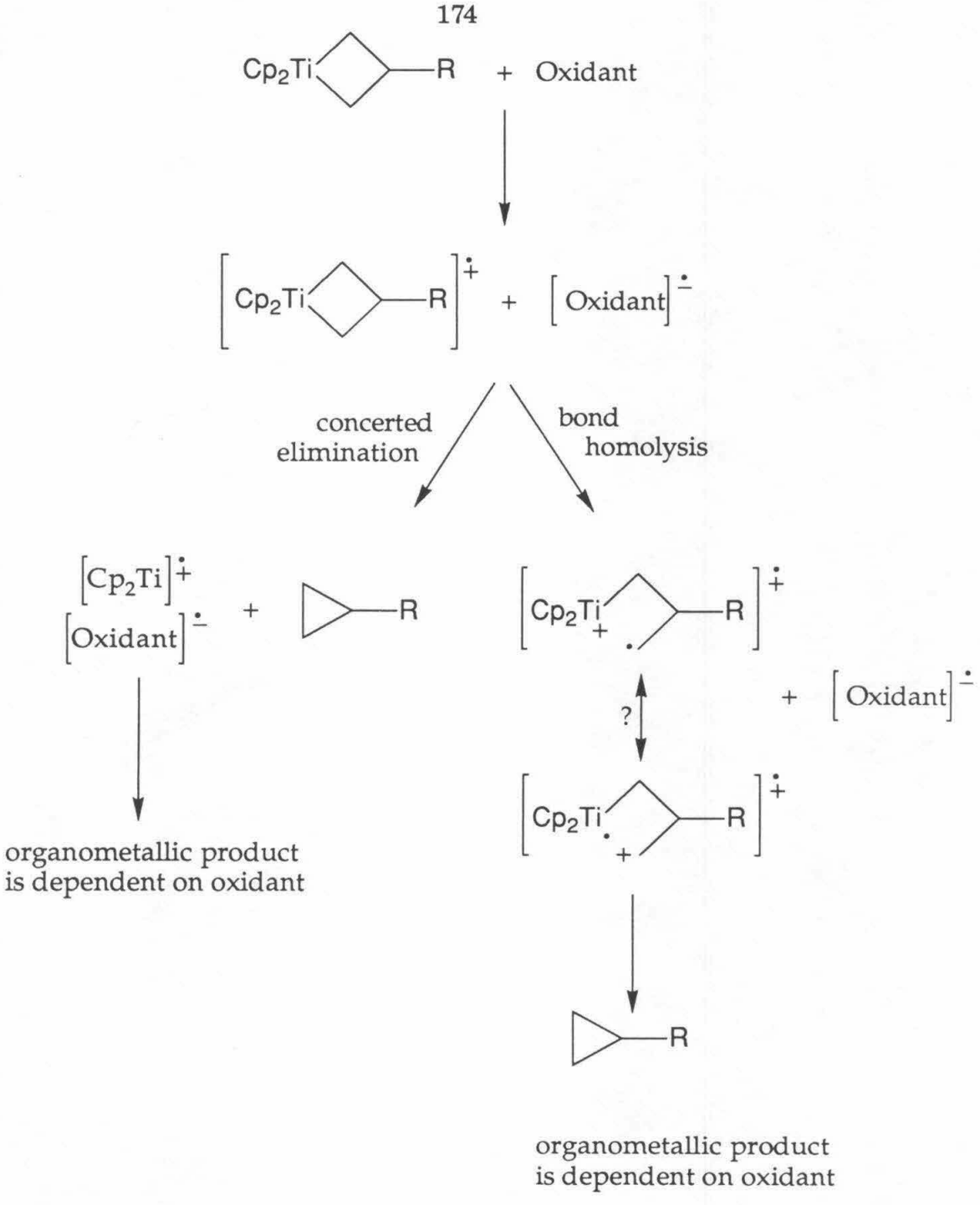


Figure 8. Concerted vs. stepwise reaction mechanism.

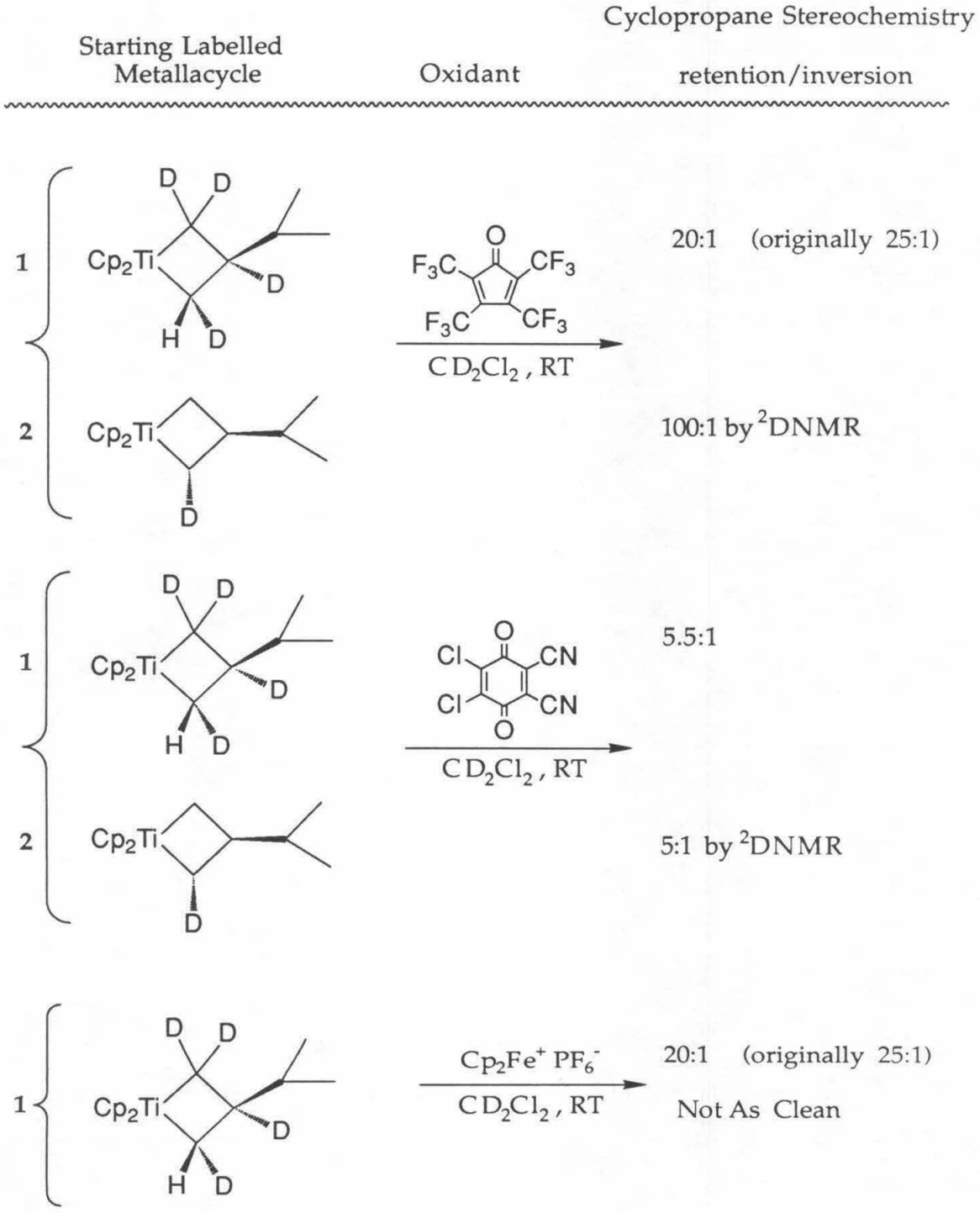


Figure 9. Stereochemical results.

Interestingly, the stereochemical ratio changes when other oxidants are employed. For example, oxidation of **2** with 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one cleanly affords cyclopropanes, which by ^{2}D NMR are >100:1 retention:isomerization. Repeating the reaction with **1** using ^{1}H NMR to examine the stereochemistry of the cyclopropane generated also indicated that retention exceeded isomerization to the extent of >80:1. The actual stereochemical result observed was 20:1 retention:isomerization; however, the starting metallacycle was only 25:1 for the isomer indicated. These two ratios, 100:1 and 80:1 are felt to be identical within the error range associated with NMR integrations.

Oxidation of **1** with ferrocenium hexafluorophosphate also generated cyclopropane with a 20:1 isomer ratio favoring retention of stereochemistry. This again translates into an ~80:1 ratio of retention to isomerization, since the starting material was only 25:1 for the isomer indicated. The stereochemical results are summarized in Figure 9.

The reason that the stereochemistry is not the same for the oxidants examined is not entirely clear at this time. More oxidants with different oxidation potentials are being examined in the hope of further elucidating the mechanism. Only the ferrocenium cation is clearly an outer-sphere electron oxidant. The other oxidants may or may not be outer-sphere oxidants for the titanacycles. The different isomer ratios may depend on whether an inner sphere mechanism or outer-sphere mechanism were operative. Partial isomerization (as observed with DDQ) could be rationalized for an inner-sphere mechansim. An outer-sphere mechanism could favor retention (ferrocenium and 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one). If the radical cation were very rapidly fragmenting

to cyclopropane, failure to stabilize the intermediate would mean a short-lived intermediate and more retention. In an inner-sphere mechanism, coordination of the anion to the cationic metal center may stabilize the intermediate, allowing it to be longer-lived and allowing more isomerization to occur at the carbon-centered radical.

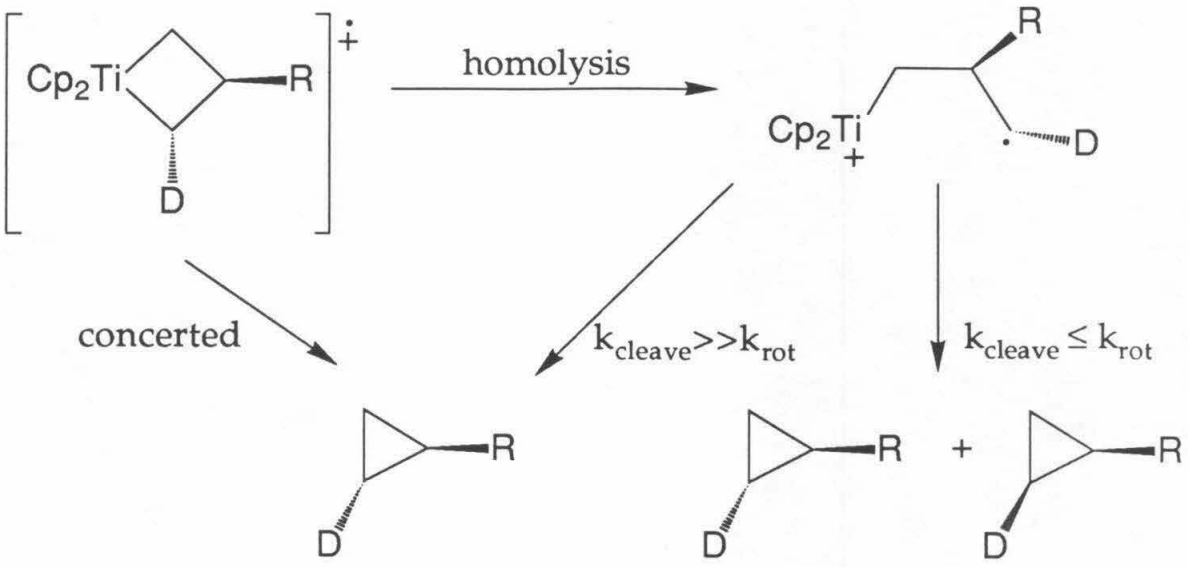


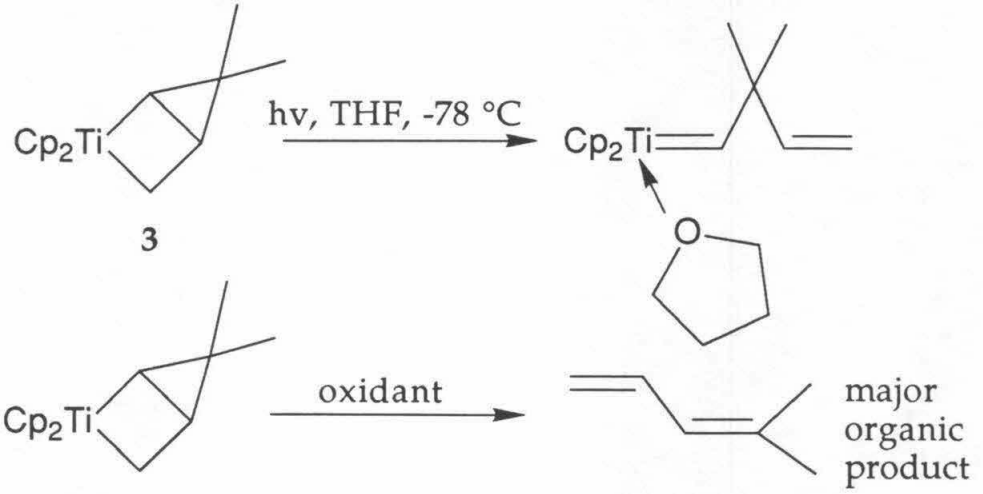
Figure 10. Possible oxidation mechanisms.

Nonetheless, these observations suggest that the mechanism of the fragmentation is either through a very short-lived intermediate, or the mechanism is concerted. If an intermediate is invoked, it must be short-lived, since none of the cyclopropanes were formed with complete isomerization (1:1 retention:isomerization). A mechanism is proposed in Figure 10. Currently, this is only speculation.

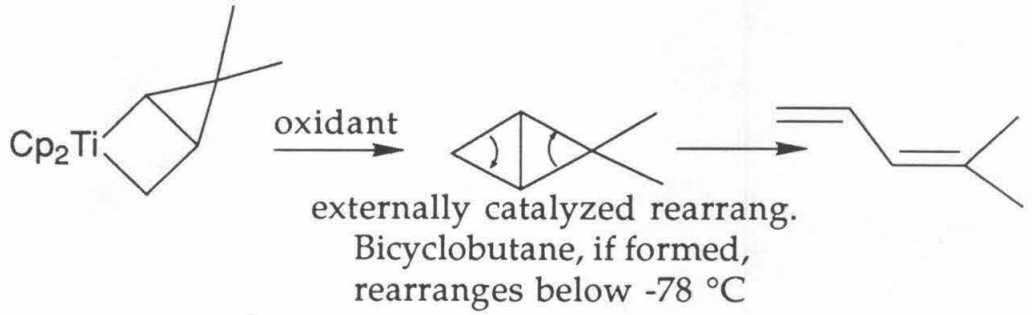
In order to further probe the reaction mechanism of this oxidation, the radical trap used in Chapter 1 was employed. The titanacyclobutane

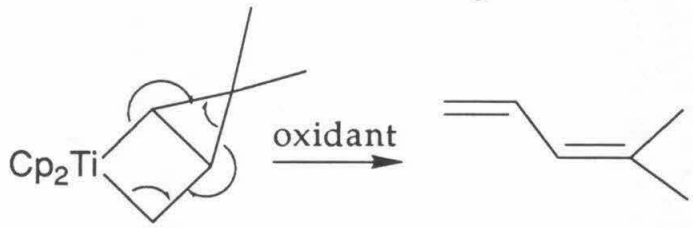
derived from titanocene methylidene and 3,3-dimethylcyclopropene, **3**, was oxidized at ambient temperature with DDQ. NMR examination of the volatiles revealed 4-methyl-1,3-pentadiene as the major product by comparison with an authentic sample. Repeating the reaction with bis(η^5-methylcyclopentadienyl)ferrocenium tetrafluoroborate and metallacycle **3** in THF at 0 °C also yielded 4-methyl-1,3-pentadiene as the major product. Traces of two other olefins were also present but could not be identified. The 4-methyl-1,3-pentadiene could be formed directly from the oxidation of **3**, or it could be formed from the transition-metal catalyzed rearrangement of an initially generated 2,2-dimethylbicyclobutane. Rearrangements of bicyclobutanes to butadienes by metals such as silver and by Lewis acids such as zinc iodide are well documented.[5] Reaction of **3** with ferrocenium hexafluorophosphate in methylene chloride at -78 °C for 4 hours followed by removal of the volatiles at -78 °C and analysis by NMR indicated 4-methyl-1,3-pentadiene as the only volatile product. This result indicates that if bicyclobutane was indeed being formed, it had to rearrange at -78 °C in order not to be observed by this technique. Therefore, it seems unlikely that bicyclobutane is formed. This set of reactions is illustrated in Figure 11.

Comparison of photochemistry and oxidation chemistry



Two Possible mechanisms:





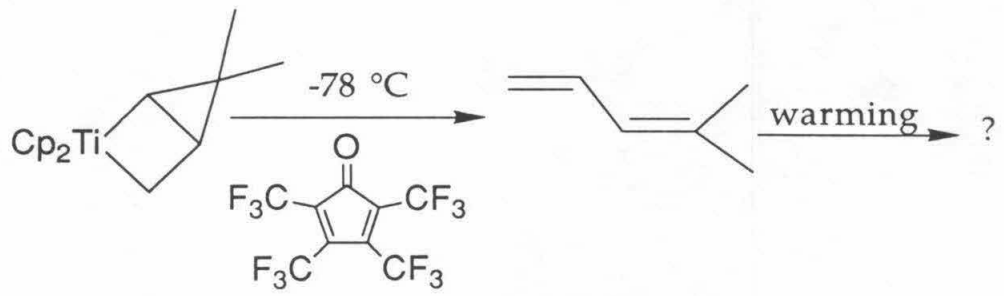


Figure 11. Radical clock oxidation.

In order to circumvent the restriction of examining only the volatiles, the reaction of **3** with 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one was investigated. Reaction of 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one with metallacycles generates, as the organometallic product, a titanium enolate, which is diamagnetic and does not interfere with NMR spectrometry, Figure 3. Reaction of **3** with 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one in toluene at -78 °C followed by warming to room temperature and NMR examination revealed that a single product was formed in 100% yield. This material is as of yet unidentified.[6] The reaction was complicated by the fact that 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one forms a charge-transfer complex with toluene. This unidentified material was observed in other solvents, too. Reaction of 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one with **3** in methylene chloride at -78 °C, followed by NMR analysis at -70 °C, indicated the presence of unreacted **3** and 4-methyl-1,3-pentadiene and the unknown compound mentioned previously. Upon warming, it was apparent from the integrations, **3** was reacting to form 4-methyl-1,3-pentadiene, which was then going on to react in some unspecified manner to yield the unknown compound. Reaction of titanium alkylidene phosphine adduct with 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one did not yield any identifiable products.

The scope of the oxidation-promoted fragmentation was examined after oxidation techniques were successfully employed to increase the yield of the reductive elimination of lactones from 2-oxa-5-oxotitanacyclohexanes.[7] Reaction of DDQ or 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one and the α-exo-methylene metallacycle (derived from a titanium methylidene and 1,1-

dimethylallene) failed to generate cleanly the expected methylene cyclopropane. Likewise, attempts to oxidize α,β-diphenyltitanacyclobutene did not yield any tractable products. It is possible that 1,2-diphenylcyclopropene was formed but was not stable to the reaction conditions. These two reactions, Figure 12, were not further examined.

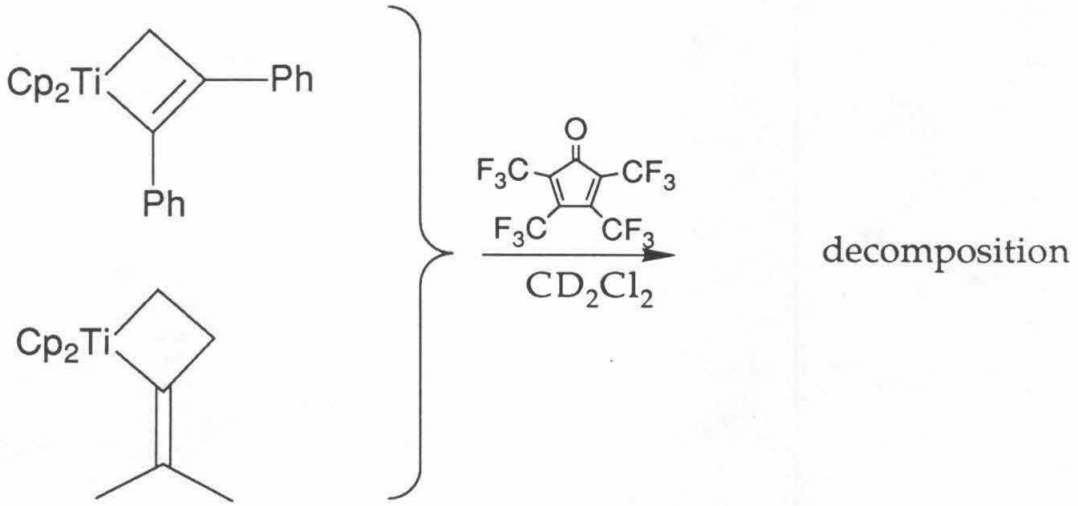


Figure 12. Unsucessful oxidations.

Examination of the oxidation chemistry of bicyclic metallacycles was much more successful. Oxidation of the metallacycle derived from norbornene and the titanium methylidene was examined in methylene chloride with a variety of oxidants. With 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one the yield of the expected product, cyclopropylnorbornene (an authentic sample was prepared from Simmons-Smith cyclopropanation of norbornene) was 91%. With DDQ the yield was 26% and with ferrocenium hexafluorophosphate the yield was 57%. The cyclopropylnorbornene was the only observed product of these oxidations.

The yields from the DDQ and ferrocenium hexafluorophosphate may be artificially low, since control experiments indicated that it was extremely difficult to vacuum-transfer the product out of the reaction mixture quantitatively. The yield of the fragmentation of the norbornene metallacycle using 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one was found to be very dependent on stoichiometry. Excess oxidant lowered the yield of the reaction. These reactions are illustrated in Figure 13.

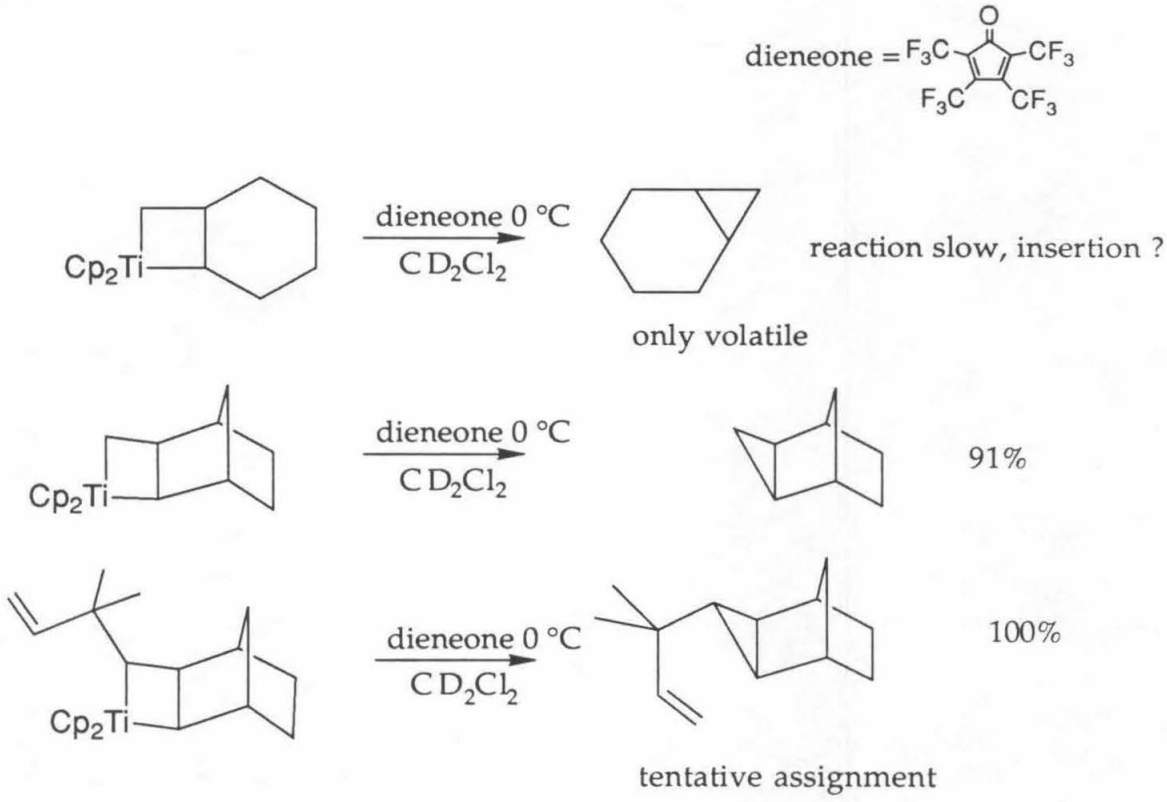


Figure 13: Oxidation of bicyclic metallacycles.

The oxidation of the thermally unstable cyclohexene metallacycle was examined using 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one, Figure 13. The only volatile product was [5.1.0] bicycloheptane in low

yield. The organometallic fraction of the reaction upon redissolving indicated that the the metallacycle was not entirely reacted. Additionally, a second product was observed, which tentatively appears to be a result of insertion of the oxidant into the titanacyclobutane ring. The low temperature at which the reaction was run explains the unreacted starting material. Another very preliminary example of insertion chemistry with 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one may have been observed in the reaction of 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one with β-dimethylsilylatitanacyclobutane. This assignment is only preliminary, and verification that these materials are correctly identified will probably require x-ray crystal structure determination.

Preliminary results indicate that the oxidation of trisubstituted metallacycles can also be achieved. It should be remembered that the trisubstituted metallacycles are photochemically inert. Oxidation of the metallacycle shown in Figure 13 with 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one provides in almost 100% yield a product that by ^{1}H NMR appears to be the product shown. The product has only 1 vinyl group and a single methyl resonance as well as only a single resonance for the norbornane ring protons, confirming that the symmetry of the product indicated is present in the sample. Further characterization is being undertaken.

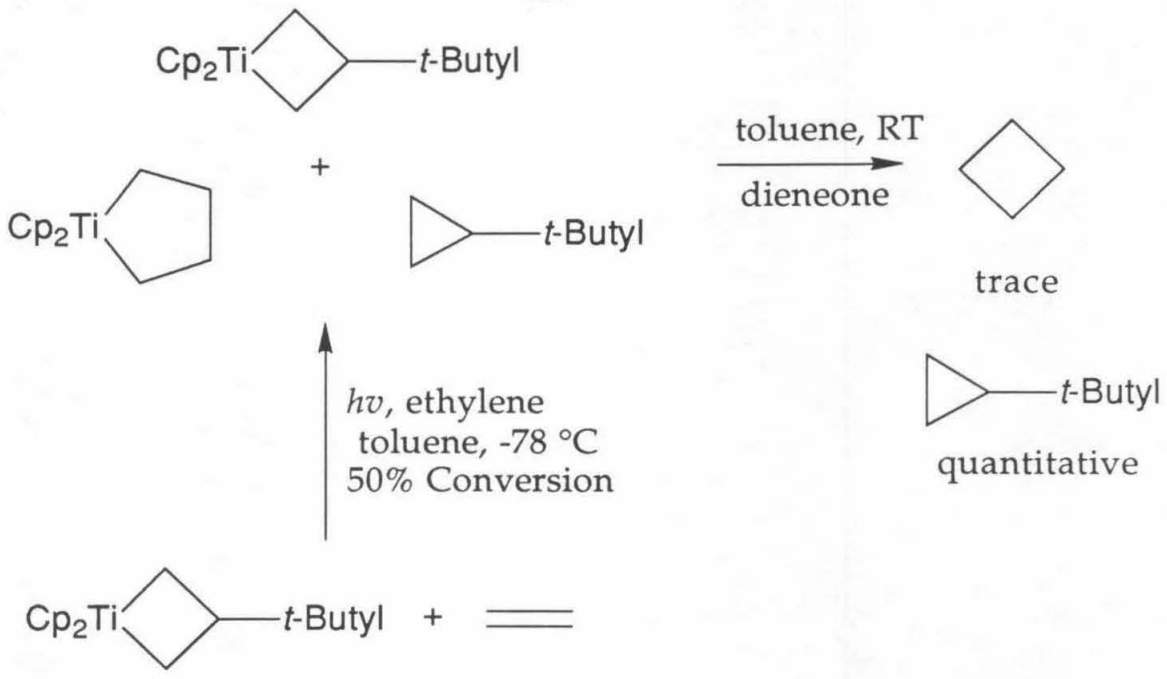


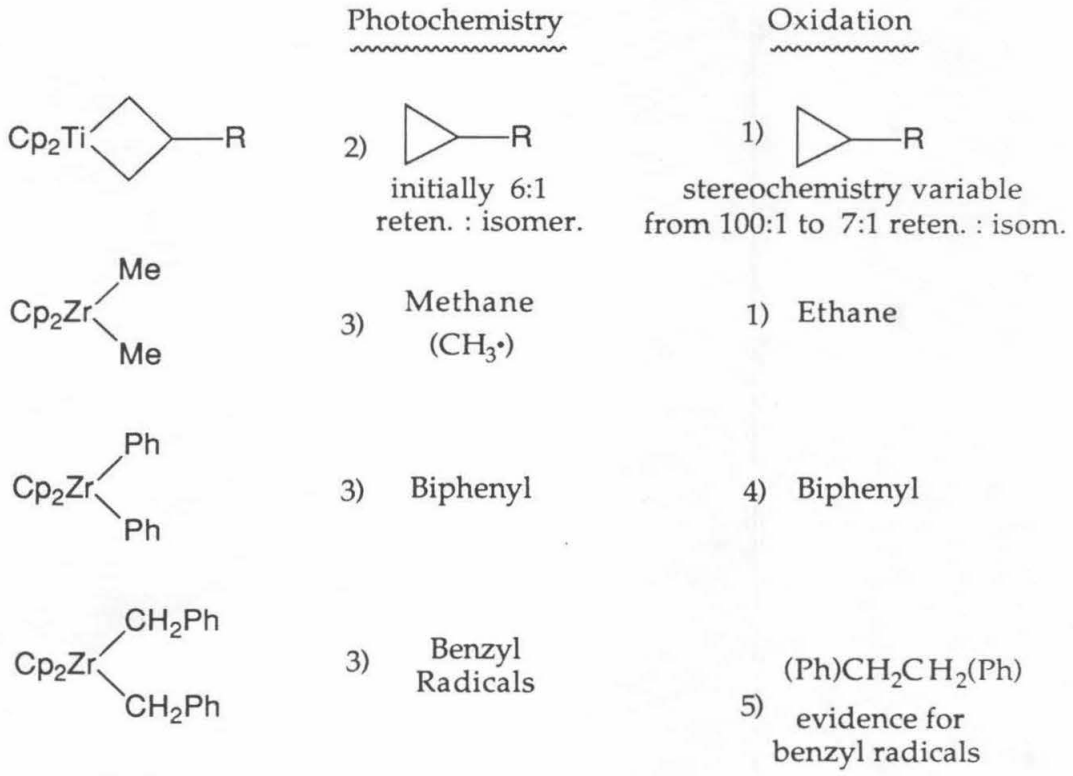
Figure 14. Preliminary oxidations of titanacyclopentane.

Preliminary examinations into the reaction of 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one and titanacyclopentane indicate that the fragmentation to cyclobutane is possible, Figure 14. Photolysis of the β-*tert*-butyltitanacyclobutane in toluene in the presence of excess ethylene yielded, upon warming, a 1:1:1 mixture of unreacted metallacycle, *tert*-butylcyclopropane, and titanacyclopentane. The oxidant was added to the reaction mixture, and after 1 hour at room temperature, the volatiles were quantitatively transferred to an NMR tube and examined by NMR. By comparison to an internal standard, the amount of *tert*-butylcyclopropane found was exactly that expected from oxidation of the remaining β-*tert*-butyltitanacyclobutane. A trace of cyclobutane was also observed. This indicates that either the yield of the reaction is very low or that the oxidation was stopped prematurely. The quantitative yield of *tert*-

butylcyclopropane indicates that the oxidation of titanacyclopentane to cyclobutane must be much slower than that of the titanacyclobutane to cyclopropane. The reaction needs to be reinvestigated at higher temperatures.

The results of the electrochemical oxidation studies are relevant to the photochemistry of titanacyclobutanes. In the photochemistry studies, the metal was formally reduced through a ligand to metal charge transfer (LMCT). Preliminary studies investigating the chemical reduction of titanacyclobutanes using sodium naphthalide, sodium potassium alloy, and electrochemical means have all yielded the same products. These products have not been unambiguously identified, but they appear to be aliphatic materials derived from reduction and protonation of the ring. Neither olefin, from retro 2+2, nor cyclopropane was observed. Concurrent with the formal reduction of the metal in LMCT, the titanium-carbon bond or perhaps the titanium-cyclopentadiene bond is formally oxidized. It is clear that the reductive elimination of cyclopropane is a result of bond oxidation, not a result of metal center reduction. Chemical reductions did not yield cyclopropanes. In the oxidation of the titanacyclobutanes, the HOMO is oxidized, followed by fragmentation to cyclopropane. The bond oxidized is likely to be a metal-α-carbon bond, not a metal-cyclopentadiene bond, or a cyclopentadiene ligand. This assumption is based on the similarity of this oxidation to the photochemistry which was presumed to proceed through an LMCT with the metal-α-carbon being the HOMO. The photochemistry possibly could be explained by cyclopentadiene to metal charge transfer followed by cleavage of the weaker metal-α-carbon bond. The same could be true of the oxidation chemistry. The metal

cyclopentadiene bond could be oxidized, followed by cleavage of the weaker bond.



1) This chapter
2) Chapter 1, this Thesis
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Figure 15. Comparison of photochemistry and oxidation chemistry for a series of zirconocenes and titanacyclobutanes.

A comparison of the photochemistry and oxidation chemistry of titanacyclobutanes and a few representative zirconocene alkyls and aryls

reveals many similarities, as shown in Figure 15. Except for the photochemically induced reductive elimination of biphenyl from diphenylzirconocene, which is considered to be concerted, the other three photochemical reactions all provide evidence of radical intermediates. The photochemically induced fragmentation appears to provide more evidence of intermediates prior to formation of the final products. The chemical oxidations do not seem to indicate the presence of intermediates as clearly, although there are indications of radicals that are even shorter-lived than the ones photochemically generated. Benzyl radicals are likely present in the oxidation of dibenzylzirconocene by ferrocenium tetraphenylborate, as evidenced by traces of the coupling product, benzylferrocene. This may be a somewhat special case since benzyl radicals are stabilized radicals. As evidenced by almost exclusive retention in the stereochemical studies and a failure to observe intermediates, the other oxidation reactions indicate that the fragmentation reaction is, if not concerted, at least faster than the photochemical fragmentation.

Photochemistry: e^- hole pair (LMCT)
Oxidation: M-R hole

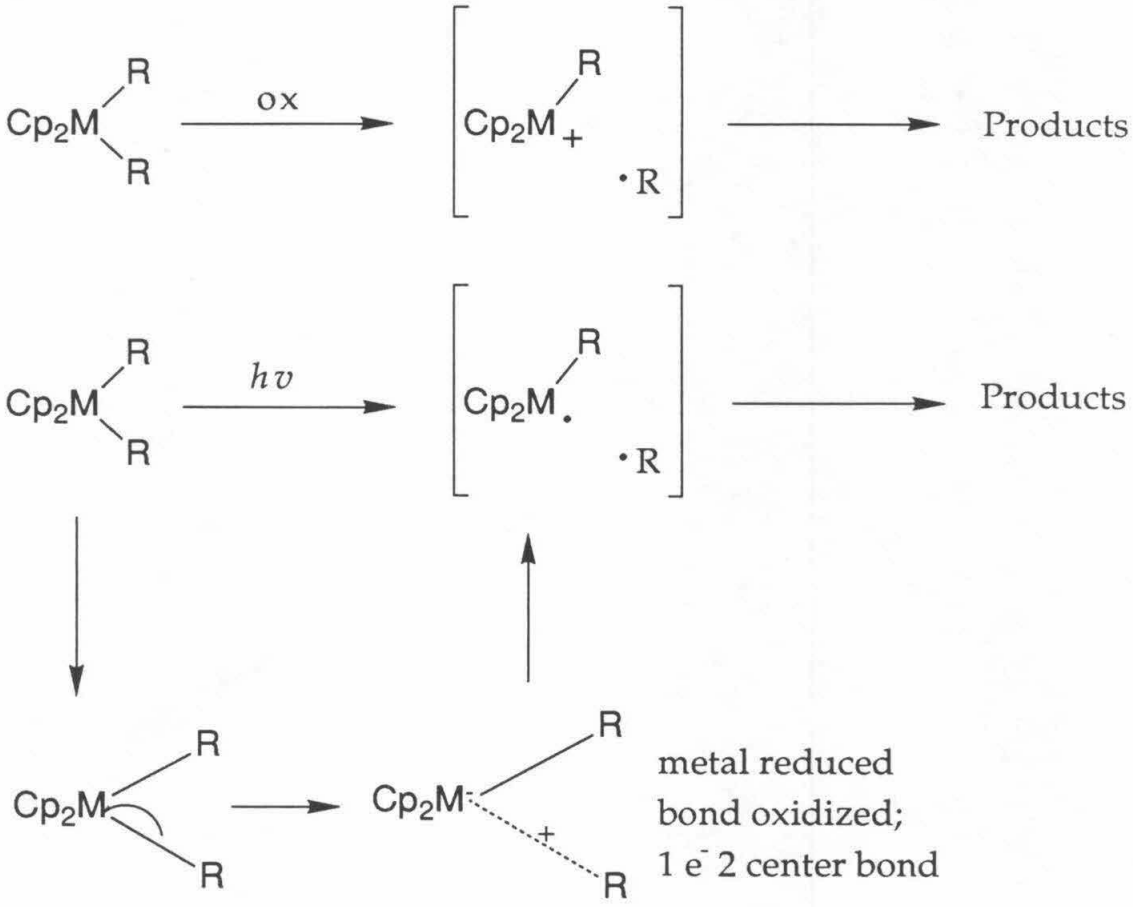

Figure 16. Similarity of the formal oxidation of a metal carbon bond by both the photochemically induced reductive elimination and the oxidatively induced fragmentation.

It is important to note that differentiation between a concerted reaction and a stepwise reaction is not always distinct, and undoubtedly many reactions fall into the gray area between these two extremes. The assignment of a reaction as concerted or stepwise is dependent on the time resolution of the mechanistic probe. Stereochemistry is a probe with resolution on the time scale of a bond rotation. Any interaction that affects

bond rotation affects the nature of the probe. Both the oxidation and photochemical experiments indicate that once the metal carbon bond is oxidized, the complex fragments and eliminates cyclopropane very rapidly. The fragmentation may be rationalized as an attempt by the metal to undergo reductive elimination and to reestablish a stable electron configuration. The photochemically generated electron hole pair and the oxidatively generated metal-carbon hole provide a unifying mechanism for understanding the formation of cyclopropanes from titanacyclobutanes.

Experimental Section:

General Procedures. All work involving air- and/or moisture-sensitive compounds was performed using standard high-vacuum or Schlenk-line techniques under argon purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Work involving manipulation of air-sensitive compounds was performed under nitrogen in a Vacuum Atmospheres drybox equipped with a -40 °C refrigerator and a dry-cool recirculator. Proton, deuterium, and carbon NMR spectra were recorded on a JEOL FX-90Q (89.9 MHz ^{1}H, 22.5 MHz, ^{13}C), and a JEOL GX-400 (399.65 MHz ^{1}H, 61.35 MHz ^{2}H, 100.67 MHz ^{13}C). Proton chemical shifts are referenced to internal, residual monoprotio-solvents. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Deuterium chemical shifts are referenced to natural-abundance deuterium in the solvent. Gas chromatography analyses (VPC) were performed on a Shimadzu GC-Mini 2 flame-ionization instrument with a 50 meter capillary column and equipped with a Hewlett-Packard model 339A integrator. Photolyses were performed with a 450 watt high-pressure mercury Hanovia lamp. Temperatures were maintained with clear pyrex dewars filled with isopropanol at the desired temperature. Temperatures cited reflect the final temperature that the bath reached at the end of photolysis; typically, a change of only 10 °C was observed. All photolyses were pyrex-filtered.

Materials. The solvents were purified as follows: toluene, benzene, tetrahydrofuran, and diethyl ether were vacuum-transferred from sodium benzophenone ketyl into solvent flasks equipped with Teflon screw-type valves. Methylene chloride, acetonitrile, chloroform, were distilled from

calcium hydride at atmospheric pressure and subsequently freeze-pump-thaw degassed. Deuterated solvents, d_8 toluene, d_8 tetrahydrofuran, and d_6 benzene were vacuum-transferred into the reaction vessel from degassed solvent pots containing a small amount of sodium/potassium alloy. Deuterated methylene chloride was dried over CaH_2 and subsequently freeze-pump-thaw degassed. Dichlorodicyanoquinone and tetrachloroquinone (chloranil) were recrystallized from methylene chloride and stored in a drybox. Ferrocenium hexafluorophosphate was received as a gift from John Brewer. It was synthesized from the oxidation of ferrocene by sulfuric acid and oxygen, followed by metathesis of the salt with sodium hexafluorophosphate and subsequent recrystallization. 2,3,4,5-Tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one was received as a gift from Mark J. Burk (Dupont, Central Research and Development, Wilmington, Delaware) and was synthesized in a proprietary manner from hexafluoro-2-butyne and carbon monoxide with a rhodium catalyst. It was purified by sublimation. Stereolabelled metallacycles were synthesized as previously described in Chapter 1. Stereochemical studies undertaken at Dupont used the same stereolabelled titanacyclobutanes. Ethylene was polymer grade from Matheson and was freeze-pump-thaw degassed on a high-vacuum line immediately prior to use.

Standard Stereochemical Experiment: In a drybox the stereolabelled metallacycle (~10 mgs) was placed in a 10 mL round-bottomed flask equipped with a stir bar and fitted with a high-vacuum valve and adapter. The oxidant was also weighed into the flask. Typically, for DDQ and the ferrocenium salts, 2-3 equivalents were employed because of their limited solubility. If tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one was employed as the oxidant, then only one equivalent was used. On a vacuum

line, solvent was condensed into the flask. Temperatures were maintained below room temperature so that thermal chemistry was not observed. Additionally, care was taken to keep light away from the reactions, since light isomerizes the stereochemical centers of the starting metallacycles. After the reaction was complete, the volatiles from the reaction mixture were vacuum-transferred into an NMR tube and the spectrum recorded. The course of the reactions could not be followed directly in the initital NMR tube because of the paramagnetic nature of the products and to the heterogeneous nature of the reaction.

Typical Oxidation Experiment: In a drybox an NMR tube was charged with the desired titanacycle. A volatile internal NMR standard was then chosen such that its resonances in an NMR spectrum did not overlap with that of the starting material. Solvent was added by syringe in the drybox and the tube was stoppered with a latex septum. Solvent was added by syringe in the drybox and the tube was stoppered with a latex septum. Outside the drybox the septum was sealed with parafilm and the NMR spectra were recorded. The tube was returned to the drybox and the desired oxidant was added to the tube. The reaction was allowed to proceed at the desired temperature. The volatile components of the reaction were then vacuum-transferred into another NMR tube. Additional deuterated solvent was added to the remaining organometallic materials. The NMR spectrum of both tubes was then recorded. The ratio of the starting material to the internal standard and the ratio of product to internal standard were used to calculate the yield of the reaction. If the oxidant was tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one, then the volatiles did not need to be vacuum-transferred to another NMR for analysis. This is because the tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-one is extremely

soluble, and the resulting products are typically diamagnetic product. If the reaction was paramagnetic, then the volatiles were vacuum-transferred as before.

References

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[1]Most of the titanacyclobutanes and all of the stereolabelled titanacyclobutanes were synthesized as described in Chapter one and were supplied by the author.

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[6] ^{1}H NMR: (toluene d_8) δ 4.24, d, 1H, J_{HH}=10.0 Hz; 2.09, m, 1H; 1.70, pseudo t, 1H, J_{HH}=9.5 Hz and 8.2 Hz; 1.39, s, 3H, methyl; 1.29, s, 3H, methyl; 0.54, dd, 1H, J_{HH}=12.7 Hz.

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